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The Photographic Image.

A

THEORETICAL AND PRACTICAL TREATISE

OF THE

DEVELOPMENT

IN THE

Gelatine, Collodion, Ferrotype and Silver Bromide
Paper Processes

BY

P. C. DUCHOCHOIS, *Photographer.*

The development is in reality an art and a science combined: the *Art* consists in getting gradation, the *Science* in making your solutions to obtain it.

Captain W. DE W. ABNEY.

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NEW YORK:
PRESS OF WILLIAM R. JENKINS,
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P R E F A C E .

We have endeavored to give in this work all the theoretical and practical instructions necessary to guide one in the operation of developing the photographic image, and we have described the processes employed to finish the clichés which is the complement of the operation.

We were led to write it for the reason that in the text-books published since a few years the development, although well described, is not treated, we think, with the importance it merits. It does not suffice to give formulas and to explain their use in some cases, their applications should be illustrated by examples, from those examples simple rules should be deducted and the special action of each of the chemicals employed must be pointed out in order that one understands

PREFACE.

the results to which give rise the modifications made in the constitution of the developing solution.

Not too many instructions can be given, for the development *is* the most difficult operation of photography, the value of the negative clichés and, as a consequence, the perfection of the pictures depending from the manner the latent image has been developed.

Indeed, it is among many amateurs and even professional photographers a common error to think that it can be done in a sort of mechanical or automatic way as it has sometimes been presented. There are probably not two subjects which can be well photographed by operating exactly in the same manner; and, to meet the various cases which present themselves, not only should the operator have studied the relation of the exposure-time to the lighting, or oppositions of lights and shades, and that of the development to the lighting, but, to the latter end, have a perfect knowledge of the action of the chemicals constituting the developing solution on the parts of the photo film impressed by light.

PREFACE.

Therefore we have written a purely theoretical chapter on the behavior of the chemicals employed, which we consider as a very important one and of which we recommend the lecture even to those having no notion of chemistry : for the theory is the base of practice—it explains the phenomena, it guides the operator ; without knowing the principles one may occasionally produce excellent works, but generally the results are imperfect, and whenever one meets with failures, he is unable to trace them to their real cause.

We present this work to those interested in the art of photography, trusting it will smooth the path to the beginners and be useful to those who desire not to work in a mechanical manner.

P. C. D.

New York, October, 1891.

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INTRODUCTION.

When a photo-plate is exposed in the camera obscura for a period of a few seconds, then treated by a reducing agent, *the developer*, one obtains a negative cliché representing the luminous image formed at the focus of the lens. The light has therefore impressed the silver salt, but the impression is not visible and cannot by any known means be detected before the development.

What is this primary action of light on the silver haloid: is it purely physical, or one causing a partial or entire reduction? It is an open question.

Although experiment shows that the ultimate luminous action results in a more or less complete dissociation of the constitutive elements, the successive changes occurring

during the period of exposures *in the camera*, which give rise by development to a negative, then to a positive, then to a negative, then again to the same series of transformations, as well as the evalescence of the luminous impression, sustain the hypothesis of a purely physical action : the silver haloid changing of state by displacement of the molecular centers and the caloris producing the work necessary to effect the chemical changes occurring in the development.

From the behavior of light on the silver haloids it results that the change goes on increasing to a certain limit which, in one way, coincides with the maximum of action producing, by development, the greatest opacity of reduction, then as the luminous action progresses the reversal commences and causes a reduction which becomes less and less opaque. This phenomenon is termed *solarization*. It was first observed by Möser, of Königsberg.

The solarization is the cause of many

defects ; thus, the sky in landscape, for example, is devoid of opacity in the negative and, as a consequence, represented by tinted whites in the positive. Furthermore, if the sky was cloudy, the clouds will not be reproduced : the half lights always disappear in the solarized high lights to which they become equal in intensity.

There are necessarily various degrees of polarization, and it is on this account that the reversal is a phenomenon useful in photography. It permits one to reproduce the ensemble of the object ; without it, it would be impossible to photograph any object with gradation from light to shade, for not only the less refrangible rays act with much less energy than the others, but even the weak lights from the same ray does not, in proportion, impress the photo-film as rapidly as the unmitigated ray. In fact the photo-film is impressed by the white light reflected from the surface of bodies, and the colored rays reflected by the body itself. Hence the rule to over expose.

During the period of over exposure the reversal necessarily commences in the high lights, that is on the parts of the photo-film upon which are projected the most luminous rays of the object, while, the action progressing on those which correspond to the half lights or tints, the latter acquire a great tendency—almost as great as that of the high lights—to be acted on by the developer, the result being, therefore, when the subject is lighted by great oppositions of lights and shades a perfect, or, at least, as possible a perfect picture as one can obtain, and if the subject is normally lighted, a picture wanting in contrasts and solarized in the high lights, that is, devoid of half tints, the whole having been equalized, so to speak, during the reversal of the primary action on the parts in question.

On the other hand, if the exposure time is short, the half lights, being in proportions to the high lights little impressed* or not at

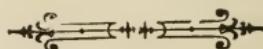
* The effects of solarization are much attenuated by dying the photo film, (orthochromatic plates).

all, fail to develop or do not take a proportionate and sufficient opacity, and the result is a picture with exaggerated contrasts unless the subject be uniformly lighted when the picture will be improved by the greater oppositions between the lights and shadows resulting thereof.

As it is seen the character of the picture can be altered by varying the time of exposure. In practice this is sometimes of difficult application, and had we not at our disposal the means to annul, or, more correctly, to attenuate the defects arising from over or short exposure-times, it would be a matter of chance to obtain perfect pictures. These means we find them in the manner of conducting the development and of compounding the developing solutions either to force the half lights to develop before the high lights gain intensity or to cause the latter to intensify to a certain extent before the former make their appearance. In a word the operator by a proper management of the chemicals can

obtain at will, so to say, either softness and harmony, or vigor and brilliancy.

Hence the perfection of the picture depends not only of the exposure-time but also, and *principally*, of the development. This is the most important operation of photography. It requires judgment and artistic taste to produce photographs of faultless beauty, and much experience to overcome the difficulties which present themselves. We hope that the beginner guided in his first essays by the general rules given in this book with examples of their applications will soon master them.



PART I.

CHEMISTRY OF THE REAGENTS.

ILLUMINATION OF THE DARK ROOM.

THE EXPOSURE TIME.

CHAPTER I.

CHEMISTRY AND BEHAVIOR OF THE COMPOUNDS EMPLOYED TO DEVELOP THE PHOTOGRAPHIC IMAGE.

SALTS OF IRON.

The following iron salts are employed in the development of the latent image : Ferrous sulphate, ferrous oxalate, and ferrous citrate.

FERROUS SULPHATE, Fe S O_4 . Syn: *proto-sulphate of iron, green vitriol, copperas.* Ferrous sulphate crystallizes with 7 molecules of water ; it therefore contains per cent 54.68 parts of the anhydrous salt.

The crystals are greenish-blue when the salt crystallizes in an acid solution, and emerald green if the solution contains ferric sulphate.

It is not venomous. Its test is styptic ; its reaction strongly acid. All the oxidizing agents transform it into ferric sulphate.

It is insoluble in absolute alcohol. Alcohol at 50° dissolves about 3 per cent. of it.

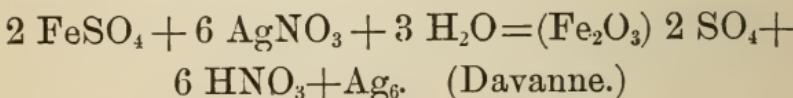
100 parts of water at { 10° C. dissolve 61
15° C. " 70
33° C. " 151 } parts of ferrous sulphate.

100 parts of ferrous sulphate { 164 parts of water at 10° C.
143 " " 15° C.
87 " " 24° C.
dissolve in 66 " " 43° C.

Exposed to the air the crystals effloresce and become covered with an ochreous coating of basic ferric sulphate, $(\text{Fe}_2\text{O}_3)_2\text{SO}_4$. This oxidation is prevented by the presence of sugar, glucose, etc.; the oxygen acts then on the organic substance by means of the sulphate which serves of a vehicle.

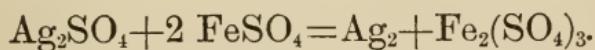
The solution of ferrous sulphate oxidizes in the air by absorption of oxygen with formation of basic ferric sulphate and normal ferric sulphate. Saccharine substances and sulphuric acid prevent these actions.

Ferrous sulphate precipitates the soluble salts of silver and gold to metal.

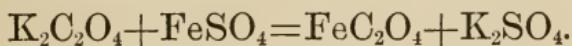


FERRIC SULPHATE, $\text{Fe}_2(\text{SO}_4)_3$. Syn.: *iron sesquisulphate*, *Monsel's salt*. Ferric sulphate is

very soluble in water. It dissolves metallic silver forming argentic and ferrous sulphate. This property is utilized in photography to reduce the intensity of negatives. The solution saturated by the aid of heat deposits, in cooling, very fine crystals of metallic silver, ferric sulphate being regenerated, thus :



FERROUS OXALATE, FeC_2O_4 , is obtained by dissolving iron in oxalic acid, or by exchange of sases by treating ferrous sulphate with neutral potassic oxalate :



It crystalizes in small, brilliant, yellow crystals. It reduces the salts of silver, but being scarcely soluble in water it is employed united to the potassic oxalate with which it forms a soluble double salts, $\text{K}_2\text{Fe}(\text{C}_2\text{O}_4)_2$. 100 parts of a saturated solution of potassium oxalate* dissolve 12 parts of the salt in question.

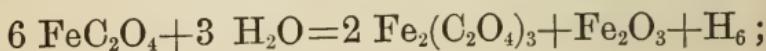
The use of ferrous oxalate as a developer was suggested by Mr. Carey Lea in 1877. The

* Potassium oxalate dissolves in 3 parts of cold water.

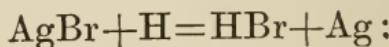
developing solution is prepared by adding 1 part of a solution of ferrous sulphate at 30 per cent of water to 3 parts of a solution of neutral potassium oxalate at the same strength.

The reduction of silver haloids by ferrous oxalate is effected by the dissociation of the elements of water. The chemical actions occurring during the reduction are as follows:

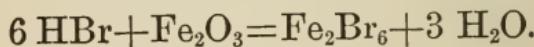
1st, The ferrous oxalate is oxidized with formation of ferric oxalate and ferric oxide in displacing the oxygen, hydrogen being set free :



2nd, Then the hydrogen in the nascent state reduces the silver salt by combining with bromine :



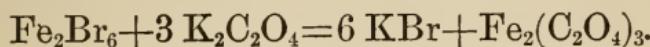
3rd, And hydrobromic acid uniting with the ferric oxide forms ferric bromide and water :



The ultimate result is represented by the following equation :



With potassium ferrous oxalate, potassium bromide is formed :



The chemical actions taking place during the development with pyrogallol, hydroquinone and other developers are similar: the reduction of the silver haloid is effected through the agency of hydrogen dissociated from water uniting to the haloid.

FERROUS CITRATE, $\text{Fe}_3(\text{C}_6\text{H}_5\text{O}_7)_2$, is prepared by double decomposition for photographic use. It was selected by Eder and Pizzighelli for the development of emulsion with silver chloride* as acting less energetically than ferrous oxalate. It is now little used. Three stock-solutions should be at hand to compound the developer, viz.:

A. *Ammonium citrate solution.* Dissolve by the aid of heat 600 grains of citric acid in $4\frac{1}{2}$ ounces of water, and neutralize by aqueous ammonia; drive out the excess of ammonia by heating, then dissolve 400 grains of citric acid and add water to make up 9 ounces.

* This emulsion is used for transparencies. Negatives can also be made with the same.

B. *Ferrous sulphate solution.* 1 to 3 of water with a few drops of sulphuric acid to prevent oxidation.

C. *Sodium chloride Solution.* 1 to 30 of water.

To develop, these solutions are mixed in the following proportion :

A	.	.	.	30
B	.	:	:	15
C	.	.	.	3

Sodium chloride is an energetic restrainer. It should be employed judiciously. The ferrous sulphate solution employed in greater proportion than that above given retards the development.

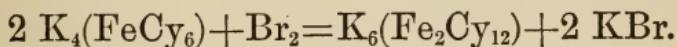
By diluting the developer less intensity is obtained, which in case of under exposures, etc., is advantageous.

Gallic acid added to the developer produces a sepia tone and acts as an accelerator. To the above solution 5 parts of a saturated solution, can be added.

POTASSIUM FERROCYANATE, $K_4(FeCy_6)$. It crystallizes with 3 molecules of water in yellow prisms or tables insoluble in alcohol, soluble in 4 parts of cold water. Its taste is

sweetish at first, then salted and bitter. It is not poisonous.

Chlorine, bromine, dilute nitric acid, all the oxidizing agents capable of displacing potassium transform it into ferricyanate :



The silver salts—chloride, bromide, nitrate—decompose it with formation of the double cyanide of potassium and silver under the influence of heat.



Potassium ferrocyanate was recommended by Mr. A. L. Henderson in conjunction with the pyrogallol developer. It is also employed with hydroquinone and eikonogen. *Per se* it possesses no reductive property. Some authors assert that it causes a softer image to be developed, others, amongst which Mr. E. Himly who studied his action with hydroquinone, that the addition of a few drops of a solution of the salt at 30 per cent of water is advisable to obtain more contrasts. The author of this book has ascertained that it effectively prevented fogging and consequently acted as a weak restrainer, but thinks that in

the whole it can be discarded, moreover, any change advisable in the character of the negatives is easily effected by compounding the developing solution with more or less reagent or more or less alkali and the usual restrainer KBr.*

POTASSIUM FERRICYANATE, $K_6(Fe_2Cy_{12})$, crystallizes without water of crystallization in rhomboidal crystals of a ruby-red color, unalterable in the air and soluble in $2\frac{1}{2}$ parts of cold water, the solution under the influence of light depositing a blue powder with formation of ferrocyanate. In presence of organic matters it is likewise reduced.

It attacks zinc, copper, lead, mercury, silver which it transforms into ferrocyanate, being itself reduced to a similar compound. This

* We have used as an energetic developer :

A.	Sodium sulphite,	40 parts.
	Potassium ferrocyanate,	20 "
	Hydroquinone,	10 "
	Water,	480 "
B.	Sodium hydrate,	30 parts.
	Water,	480 "

Equal volumes for rapid exposures.

action is utilized for the reduction of over dense clichés (Farmer's process).

PYROGALLOL.

PYROGALLOL, $C_6H_6O_3 = C_6H_3(OH)_3$. Syn: *Tri-oxybenzine, pyrogallic phenol, pyrogallic acid.* Pyrogallol is venomous, causing death at the dose of from 2 to 3 grams in acting as phosphorous by absorption of oxygen from the blood.

It occurs in prisms or in long needles which are perfectly white.

It blackens in damp air, the action being more rapid in the light. The products of the decomposition are brown-black matters whose constitution has not been ascertained, *plus* oxalic and acetic acid and carbon dioxide :

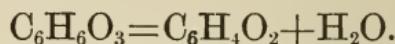


Its taste is faintly bitter, its odor nul,* its reaction neutral.† It melts at $115^\circ C.$, boils at

* The commercial pyrogallol has generally an empyreumatic odor. If it deposits a black substance it contains metagallic acid which is insoluble.

† Litmus paper turns slightly red, but assumes its original blue color in drying, exactly as when reddened by carbonic acid.

210° C., and at 250° C., splits into metagallic acid and water, thus :



Pyrogallol is soluble in $2\frac{1}{2}$ parts of water at 15° C., $1\frac{1}{4}$ part of alcohol at 90° and in $1\frac{1}{4}$ part of ether. The aqueous solution turns black in the air by absorption of oxygen, depositing black flocks and evolving carbon dioxide. Sulphurous acid, the alkaline sulphites, citric, oxalic, and formic acids, traces of nitric acid prevent this decomposition. The alcoholic solution is more stable and keeps for a long time, it being little altered.

In presence of the alkalies, of the alkaline carbonates and aqueous ammonia, pyrogallol rapidly absorbs oxygen, becomes yellowish, then brown and lastly brown-black with formation of carbon dioxide (carbonic acid), acetic acid, oxalic acid, etc., and traces of hydrogen dioxide.

It does not decompose the carbonates. Boiled with potassium hydrate pyrogallol is decomposed into carbon dioxide, acetic and oxalic acids. Added to lime water, the liquid assumes a fine red tint which turns brown.

This action is very delicate. It serves in analyses.

Hydrochloric acid has no action on pyrogallol.

Nitric acid transforms it into oxalic acid.

Nitrous acid and the nitrites even in very small quantities turn brown its solution. This action serves to detect infinitesimal traces of these compounds.

Chlorine decomposes pyrogallol in precipitating a black substance and forming hydrochloric acid.

Bromine forms an insoluble bromized derivative $\text{Br}_3(\text{C}_6\text{H}_3\text{O}_3)$ which first becomes deep red in presence of the alkalies and then turns red-brown in the air.

Ammonia precipitates from the ethereal solution of pyrogallol, white crystals of a compound termed ammonium pyrogallate $\text{C}_6\text{H}_5\text{NH}_4$, which rapidly oxidizes in the air with formation of pyrogallein.

Potassium permanganate decomposes it, liberating carbon dioxide with effervescence in concentrated solution. The permanganate is decolored.

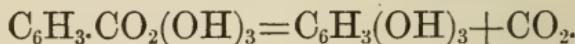
Heated with anhydrous phthalic acid, it is

converted into *gallein*, which treated by hot sulphuric acid yields a very staple green coloring matter, the *cœrulein* employed in orthochromatic photography.

Pyrogallol unites with gelatine and casein. It gives with ferric chloride a red coloration turning black progressively. It colors the skin and hairs brown-black.*

It reduces the salts of silver, gold and platinum. In silver nitrate solutions it dissociates the metal, depositing a red compound termed *purpurogallein*, $C_{20}H_{16}O_9$, which oxidizes rapidly.

Pyrogallol is obtained from gallic acid which under the influence of heat splits into carbon dioxide and the compound in question :



In manufactures it is obtained from nut-galls which yields about 12 per cent of it. The dry extract is placed in an iron vessel heated to 180° C. on a sand bath and covered with a receiver into which pyrogallol sublimes and condenses in prisms.

* Stains on the hands can be removed by a dilute solution of sulphuric acid 1.100, or of hydrochloric acid 5.100 or by citric acid or any clearing solution.

HYDROQUINONE.

HYDROQUINONE, $C_6H_6O_2 = C_6H_4(OH)_2$. Syn: *Quinol, Paradioxybenzene.* Hydroquinone is a diatomic phenol isomeric with catechol and resorcinol. It is formed by the action of dioxidizing agents such as sulphur dioxide, hydriodic acid, stannic acid, etc., on quinone which takes up a molecule of hydrogen, $C_6H_4O_2 + H_2 = C_6H_6O_2$, or by oxidizing aniline with potassium bichromate. It is by the latter process that it is produced in manufactures, thus: one part of aniline and 8 parts of sulphuric acid are dissolved in 30 parts of water and the mixture allowed to cool. Two and a half parts of pulverized potassium bichromate are then little by little added, taking care to keep cold the solution, whereby among other products hydroquinone is formed together with quinone. A current of sulphur dioxide now passed through the solution transforms the quinone into hydroquinone which is taken up by ether. The ethereal solution rises on the surface and, the aqueous liquid being drawn off, the ether by evaporation leaves a residue which is dissolved in a

small quantity of hot water, and from this solution treated by sulphur dioxide, decolorized with animal charcoal, boiled, filtered, and cooled, hydroquinone is deposited.

Hydroquinone crystallizes in orthorhombic prisms without taste and odor, and without action on test paper. When the crystallization is slow the crystals are lemon-yellow and contain 27.2 of water per 100. But if formed rapidly, they are very white and take up only 12.8 parts of water.

It is soluble in ether and alcohol. Water, at 15° C. dissolves 6 per 100 of it, and 9.5 parts at the temperature of 30° C. It melts at 169° C., and when gradually heated it sublimates easily as brilliant scales without alteration. It is on this form that it is generally found in commerce.

It reduces in the cold the salts of mercury, silver, gold and platinum with formation of quinone by elimination of hydrogen :



According to H. Reece, 8 parts of hydroquinone reduce 68.22 of silver oxide.

The reductive property of hydroquinone is

increased by the hydrates and carbonates of the alkali metals, it being transformed by oxidation into quinone, green hydroquinone and brown substances analogous to those formed by the oxidation of pyrogallol. The solution is first tinged yellow, then turns red-brown and possesses tinctorial properties. *Per se* hydroquinone does not reduce the silver haloids.

Hydroquinone is not precipitated by lead acetate. It dissolves without alteration in normal and acid sulphites solutions from which it deposits as yellow crystals containing sulphurous acid. These solutions are almost inalterable in the air and keep well even in presence of an alkali.

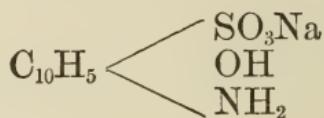
Nitric acid transforms hydroquinone into oxalic acid.

Chlorine, ferric chloride, potassium bichromate, silver nitrate and other oxidizing agents convert it into quinone and an hydroquinone crystallizing in needles with a beautiful green lustre. This compound, *Green hydroquinone*, $C_6O_5O_2$, is soluble in ether and alcohol. Sulphur dioxide resolves it into colorless hydroquinone. Treated by ammonium hydrate and

the alkalies it rapidly absorbs oxygen, being converted into a red-brown coloring matter.

Hydroquinone forms derivatives with the haloids. Its use in photography was suggested by Captain W. de W. Abney, in 1880.

EIKONOGEN.



This compound is the sodium salt of Amido *B*-Naphtol *B*-monosulphonic acid, discovered in 1881, by professor Raphael Meldola.

It crystallizes with 2 molecules of water in semi opaque yellowish-white crystals having a shining lustre. Its taste is sweetish and peculiar, its smell prickly. It slowly evolves acid fumes in being decomposed.

It is insoluble in alcohol, dissolves with difficulty in cold water which, however, retains at common temperatures from 7 to 8 parts per cent when the solution has been effected by heat. According to a well known law of chemistry, it is precipitated from its solution by the addition of a more soluble salts, sodium

sulphite, carbonate, etc. We found that in an aqueous solution containing per cent 5 parts of normal sodium sulphite only 4 parts of eikonogen can be dissolved. As pyrogallol and hydroquinone, eikonogen possesses tinctorial properties when oxidized, the dyed substance, gelatine, being greenish by reflection and pink by transparency.

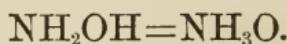
Eikonogen reduces silver nitrate in acid solutions, but *per se* it has no action on the haloid salts of that metal without the intervention of an alkali. However, the reduction takes place, although slowly, yielding very clear negatives, in presence of sodium sulphite, which may be explained by the alkaline reaction of the salt.

With an alkali to form a more reductive compound, eikonogen reduces almost instantaneously the silver haloids impressed by light; but notwithstanding such a powerful reducing action, by equal weight, it absorbs four times less oxygen than hydroquinone (H. Reeb) and still less than pyrogallol. The energy of its action is therefore soon impaired, and this explains why during the development the image, which rapidly appears in all its details

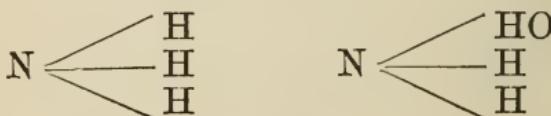
slowly intensifies, and why it should be employed in larger quantity than the other reagents to obtain strong negatives.

According to Mr. H. Reeb, 8 parts of hydroquinone make the work of 33 parts of eikonogen, these quantities reducing 100 parts of silver nitrate, or the equivalent of silver oxide, with the same dose of alkali: 40 parts of potassium carbonate or 23.53 parts of sodium hydroxide.

HYDROXYLAMINE OR OXYAMMONIA.

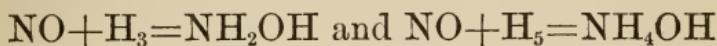


This base discovered by Lossen, in 1865, is considered as ammonia in the constitution of which a molecule of hydroxyl is substituted to one atom of hydrogen, thus :



It is formed by the action of hydrogen on nitrogen oxide. This mode of formation is similar to that of ammonia when the oxide and

hydrogen in excess are simultaneously passed on heated platinum sponges, thus :

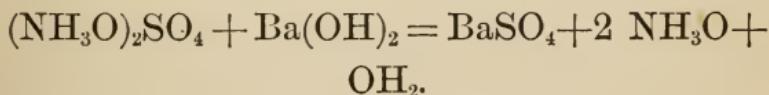


All the salts of hydroxylamine, like those of ammonium, are decomposed by the alkalies which set free hydroxylamine.

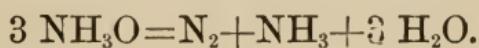
Hydroxylamine possesses powerful reducing properties. It reduces the salts of aluminum, zinc, iron, lead, silver and gold, and transforms manganese dioxide into monoxide.

It converts mercuric chloride into calomel and, in excess, precipitates it to metallic state.

Hydroxylamine has not been isolated. It is known only in solution or combined to acid radicals. A pure solution is best obtained from the sulphate treated by calcium hydrate:



It is decomposed by the alkalies into nitrogen and ammonia, the action progressing so much more rapidly as the solution is more concentrated :

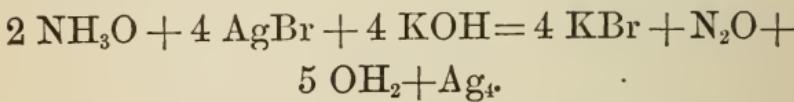


The chloride and nitrate of hydroxylamine

are soluble in water and in alcohol. The sulphate is precipitated by alcohol from its aqueous solution.

Hydroxylamine precipitates cuprous oxide from cupric sulphate in hot solutions.

As a developer in the gelatine process, hydroxylamine was suggested by Spiller and Egli, either alone or in conjunction with pyrogallol. It yields very clear negatives. The ultimate action is represented by the following equation:



In the arts it is employed in calico printing to form reserves.

For our purpose it is obtained from the chlorhydrate treated by an alkali, and acts while in the nascent state with great energy.

The chief advantage of hydroxylamine as a developer is not to absorb oxygen from the air. Its solution is therefore inalterable. It is little employed on account of the evolution of nitrous oxide, N_2O , which gives rise to blisters in the gelatine process.

THE HYDROXIDES (HYDRATES) AND CARBONATES OF THE ALKALI-METALS.

Potassium, sodium, ammonium, and lithium hydroxides are employed in the development of the latent image. Their action consists to increase the reductive power of the reagent by exalting its affinity for oxygen, but see further on.

Whatever be the hydroxide employed the ultimate result is the same.

When substituting an hydroxide for another in formulas one should take into account their equivalence which necessarily varies with that of the metal.

The following table shows the equivalences of the hydroxides :

Potassium.	Sodium.	Lithium.
KOH	— NaOH	— LiOH
56	=	40
1.	=	0.714
1.4	=	1.
1.5	=	1.666
	=	=
		24
		0.428
		0.6
		1.

Ammonium hydrate being very volatile and sold in solutions at various strengths, it is not possible to give any data for the equivalence.

The carbonate of these bases are also employed for the purpose in question. They act as the hydrates but with less energy, and not possessing so strong caustic properties, they do not disorganize organic substance so rapidly. For this reason when the gelatine film blisters with a developer prepared with the alkalies, the carbonates should be substituted.

The following table shows the equivalences of potassium and sodium carbonates:

K_2CO_2			Na_2CO_3					
Anhydrous. + 2 H ₂ O.			Anhydrous. + 10 H ₂ O. + 5 H ₂ O.					
138	=	174	=	106	=	286	=	196
1.	=	1.261	=	0.768	=	2.072	=	1.421
0.793	=	1.	=	0.919	=	1.643	=	1.126
1.301	=	1.641	=	1.	=	2.698	=	1.849
0.443	=	0.608	=	0.370	=	1.	=	0.685
0.709	=	0.887	=	0.592	=	1.459	=	1.

The ammonium carbonates are volatile. No data can be given. They are employed by few operators.

POTASSIUM HYDROXIDE or HYDRATE, KOH=56, is commonly known under the name of *caustic potash* to distinguish it from the potash of commerce which is an impure carbonate.

Potassium hydroxide is a hard, white substance possessing energetic basic property, very caustic, soluble in alcohol, exceedingly deliquescent and consequently very soluble in water.

It softens the skin and progressively dissolves it, disorganizes numerous organic matters, neutralizes all the acids and dissolves fatty and resinous substances by uniting with their acid radicals.

It decomposes glasses, especially those containing lead, and porcelain, potteries, etc., by dissociating the aluminia and the silicates. Potassium carbonate acts in the same manner.

In chemistry it is employed to precipitate the insoluble oxides from their combinations. It is the best reagent to detect the ammonium salts, liberating ammonia which is readily recognized by its characteristic smell.

POTASSIUM CARBONATE, K₂CO₃=138. This salt is white and deliquescent. In contact

with the air it absorbs carbon dioxide, being transformed into bicarbonate. It dissolves in its weight of water. To obtain a solution at .100 per 100, it should be dissolved in 100 c. cm. of water in a quantity sufficient to form a volume of 143 c. cm.

It crystallizes with two molecules of water. Its reaction is strongly alkaline. It contains per cent 54.02 parts of potassium oxide, K_2O .

There are three grades of potassium carbonate sold in commerce, viz.: *potash* which is quite impure, containing about 60 per 100 of carbonate mixed with chloride, sulphate and silicate of potassium in various proportions; *pearlash*, which is purer; and *salt of tartar* containing but a small quantity of chloride. The latter can be employed instead of the chemically pure compound.

SODIUM HYDROXIDE or HYDRATE, $NaOH = 40$. The properties of this base are similar to those of potassium hydrate, although somewhat less energetic. As the latter it is deliquescent in the air from which it absorbs carbon dioxide in being transformed into carbonate. It crystallizes with 7 molecules of water.

It is sold under the name of *caustic soda*. The soda of commerce is an impure carbonate.

The salts of sodium color the flame of alcohol yellow.

SODIUM CARBONATE, Na_2CO_3 . Sodium carbonate is white, its taste caustic and acrid, its reaction strongly alkaline. It crystallized with 10 molecules of water of which it loses 5 in efflorescing in the air. Crystals with seven molecules of water are obtained from the mother waters of crystallization of the compound with 10 H_2O .*

The crystals with 10 H_2O contains 62.94 of water per 100

“	“	“	7 H_2O	“	54.31	“	“
“	“	“	5 H_2O	“	45.92	“	“

100 parts of water at
the temperature of $\left. \begin{array}{l} 14^\circ \text{ C. dissolves } 16.65 \text{ parts of salt.} \\ 20^\circ \text{ C. } “ 25.83 “ “ \\ 30^\circ \text{ C. } “ 30.83 “ “ \end{array} \right\}$

It is insoluble in alcohol.

The sodium carbonate of commerce—washing soda—is very impure, containing about 3 per 100 of various salts: sulphite, thiosulphate

* For this reason the commercial article contains variable quantities of water of crystallization.

(hyposulphite), silicate, chloride, and sometimes traces of cyanide, ferrocyanide, sulphocyanate, besides iron and lead oxides.

AMMONIUM HYDRATE, $\text{NH}_4\text{OH}=35$. This is one of the most energetic bases. Its fumes are suffocating. They are neutralized by acetic acid.

The aqueous solution concentrated at 26° Baumé contains 35 per 100 of gaseous ammonia. The solution is not permanent. The water gives off all the gas when heated to 60° C., or, gradually, in open vessel at ordinary temperatures. In contact with the air it absorbs carbon dioxide, being converted into carbonate.

The concentrated solution of ammonia dissolves without alteration chloride and bromide of silver, the latter sparingly.

Ammonia forms with iodine, silver oxide, gold and platinum chlorides—dangerous compounds which explode often spontaneously or under a slight friction.

Ammonia is employed to cauterize the bites of venomous reptiles, bees, etc., to dissolve carmine, to clean clothes by mixing it with two

parts of alcohol. As a base; it is employed to instantly neutralize the fumes of acids and their disorganizing action on the skin and on cloths and fabrics, of which it generally revives the color if applied at once.

AMMONIUM HYDROGEN CARBONATE (BICARBONATE), HNH_4CO_3 . This salt spontaneously evaporates in the air, emitting the characteristic odor of ammonia. It is insoluble in alcohol, soluble in 8 parts of water to which it imparts a strong alkaline reaction. Heated to $36^\circ \text{ C}.$, it is decomposed with evolution of carbon dioxide. Boiling-water decomposes it.

The carbonate of ammonia of the druggists, commonly termed sesquicarbonate, is a mixture of bicarbonate and carbamate of ammonium, $\text{HNH}_4\text{CO}_3 + \text{NH}_4\text{CO}_2\text{NH}_2$.

AMMONIUM SESQUICARBONATE, $\text{H}_2(\text{NH}_4)_4(\text{CO}_3)_3$. The reaction of the sesquicarbonate is strongly alkaline, its taste caustic and its odor ammoniacal. It crystallizes in transparent octahedral prisms with 4 molecules of water. It is unstable, rapidly evolving ammonia in being transformed into bicarbonate.

25 parts dissolve in 100 parts of water at 13° C.

30 " " " " " 17° C.

37 " " " " " 32° C.

What are the actions of the alkalies in the development?

The principal action is, as we have said, to increase the property of certain developers to absorb oxygen and, thereby, to possess a more energetic reducing action. That needs no comment; it is a scientific fact. But besides this and neutralizing the hydracids formed by the reduction of the silver haloids, there is a secondary action which is most important, occurring with every reagent, and permitting one to conduct the development at will, so to say.

It has been shown by Mr. Henry T. Anthony (June, 1862) that when a dry plate is exposed to gaseous ammonia before being subjected to the luminous influence, its sensitiveness is increased considerably—this was the starting point of the alkaline development—and Dr. von Monckhoven has demonstrated that ammonium hydrate, a caustic alkali, acts on silver bromide as does heat when preparing the

emulsion, that is, causes certain changes in the molecular arrangement of the constitutive elements of the salt, Ag and Br, which renders the salt exceedingly sensitive to light. Therefore it is admissible, and experiment proves it, that the alkalies act somewhat in a similar manner during the development and predispose the silver haloids to dissociation.* The whole silver film is necessarily acted on, and if the alkali be in great excess a general reduction takes place before the details and density are obtained. This is termed fogging. But when employed at certain doses to act independently from the reducing agents to which they unite and of which beyond a certain limit they do no more as a consequence increase the reductive property,† the alkalies if not enough powerful to cause a general reduction, act, however, on the parts already modified by light. Therefore the parts impressed by weak lights—those forming the half-tints of the picture—acquire a greater tendency to

* A boiling solution of potassa or soda converts silver-chloride into oxide which is rapidly reduced to metal by sugar, glucose, etc.

† See Pyrogallol.

reduction, and if the reductive power of the developer is not energetic, as it happens when the reagent is employed in small proportions, these parts in presence of free alkalies will develop sometimes simultaneously with the most impressed, and in every case, except when the exposure is insufficient, before the latter acquire a great intensity.

The reader should bear in mind these actions of the alkalies; their judicious applications during the development are of the greatest importance to obtain good negatives.

The carbonates act necessarily with less energy than the caustic alkalies and permit to increase the dose with less danger of producing fogging or blistering.

The alkalies—caustic ammonia excepted—act too energetically with pyrogallol which then, by rapidly absorbing the atmospheric oxygen, soon exhausts its reductive power.

For 1 of pyrogallol $1\frac{1}{2}$ parts of K_2CO_3 is a normal dose; 3 parts is a large dose; 5 parts is a maximum. Water, 100 parts.

For 1 of pyrogallol 2 parts of Na_2CO_3 is a

normal dose; 4 parts a large dose; 6 parts a maximum. Water 100 parts.*

For 1 of hydroquinone, dissolved in 100 parts of water, from 3 to 15 parts of Na_2CO_3 have been employed. Bouillaud uses for instantaneous exposures as much as 25 parts, and 6 of sodium sulphite.

With the same quantity of hydroquinone from 3 to 12 parts of K_2CO_3 or from 1 to 4 parts of caustic soda are used. Himly compounds the bath with 2 parts of hydroquinone, 14 parts of sodium sulphite, 7 parts of NaOH and 100 parts of water.

When using large doses of alkalies it is advisable to add a restrainer, say, $\frac{1}{2}$ part of potassium bromide per cent.

THE SULPHITES.

NORMAL or NEUTRAL SODIUM SULPHITE, Na_2SO_3 , crystallizes with 10 molecules of water, but more often with 7 molecules. The former consequently contains per cent 58.82 parts of water and the latter 50 parts.

* At the same dose potassium carbonate acts more energetically than the sodium salt on the silver haloids.

This salt is white, its taste *sulphurous*, not bitter and nauseous as that of sodium thiosulphate (hyposulphite).* It dissolves in 4 parts of cold water and its weight of boiling water. The anhydrous compound dissolves in 7.07 parts of water at 0° C., in 3.35 parts of water at 15° C., and 2 parts of boiling water. All these solutions are alkaline. They dissolve silver chloride and bromide forming double salts, which can be employed for silvering. For this purpose a strong solution of silver nitrate is gradually added to another of acid sodium sulphite (bisulphite) until the precipitate dissolves with difficulty, but dissolves. This is a very good and industrial process, for it permits one to obtain a thicker silver deposit than by most of the other compounds. Roseleur gives the following proportion : 1 AgNO₃ : 6 Na₂SO₃.

The silver solution may also be used for the intensification of negatives previously treated by mercuric chloride.

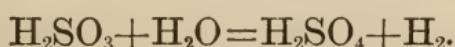
* These two salts are easily distinguished from each other by adding to their solution a small quantity of sulphuric acid, or any other one, sulphur being set free if the salt is a thiosulphate. The solution of the sulphite remains clear. Both evolve sulphur dioxide.

Normal sodium sulphite either in crystals or in solution absorbs oxygen from the air, being gradually transformed into sulphate.

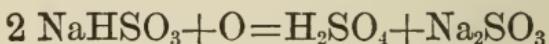
With the exception of carbonic, hydrocyanic and boric acid, the hydracids, sulphuric acid, formic and citric acids decompose it evolving sulphur dioxide by uniting to sodium. Nitric acid converts it into sulphate with formation of nitrous fumes, NO_2 .

Sodium sulphite is employed as an anti-chlore and to destroy ferments.

In photography it is employed : 1st, to avoid the rapid oxidation of the reagent resulting from its absorption of the atmospheric oxygen : the sulphite having a greater affinity for oxygen than the reagents, takes it up from the air, so that the oxidation of the developer only results from the nascent oxygen dissociated during the development ; and, 2nd, to prevent the dyeing of the film by its deoxidizing action ; or, what is more generally admitted, by causing the formation of an incolorous compound of the dye with the hydrogen liberated from the elements of water, thus :



For keeping, the developers are best prepared with the hydrogen or acid sodium sulphite (bisulphite), NaHSO_3 , whereby the oxygen does not act on the sodium salt, but on the sulphurous acid which is converted into sulphuric acid. The acid then acts on the sodium sulphite, liberating sulphurous acid which in its turn undergoes a similar change, thus:



and $\text{Na}_2\text{SO}_3 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_3$, etc.

Sodium sulphite can exalt the reductive properties of pyrogallol sufficiently to develop the latent image. The development is slow and yields clear negatives. The sulphites also prevent fogging when added to hydroquinone.

This energetic action imparted to the developer does not depend from the carbonate which the commercial sulphite always contains, for the chemically pure salt behaves in the same manner.

According to Captain Abney, sodium sulphite forms a very oxidizable compound with pyrogallol. This and the alkaline reaction of the salt account for the phenomenon.

Sodium sulphite does not act so with hydroquinone. The mixture is incapable of effecting the development of the image. But it does with eikonogen, probably by preventing this salt to exhaust its reductive action by absorbing oxygen from the air, for which it possesses an exceedingly great affinity.

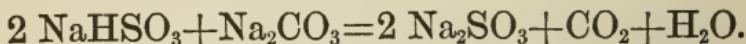
From 4 to 5 parts of sodium sulphite for 1 of pyrogallol, 3 to 4 for 1 of hydroquinone, 6 to 7 for 1 of eikonogen are sufficient to check for a certain period, long enough for the exigencies of the development, the oxidation of the reagents in contact with the air.

Ready-made developers are necessarily compounded with larger proportions of sulphite on account of the presence of the alkalies.

Many acids have been recommended to evolve sulphurous acid from the sulphite in order to keep the plain solutions of pyrogallol and hydroquinone for a long time. Such are citric, oxalic, formic, nitric, sulphuric acids, etc. The two former form with the base of the sulphite compounds which act as restrainers; the formate exerts a certain reductive action; as to the sulphate and nitrate they are

inert.* Sulphuric and nitric acid are therefore recommended. From 2 to 4 per 100 of sodium sulphite are sufficient for the purpose in question.

HYDROGEN or ACID SODIUM SULPHITE (BISULPHITE), NaHSO_3 . This salt is white and evolves the smell of sulphur dioxide. When anhydrous it is termed *metabisulphite*. It attracts oxygen from the air more rapidly than the normal salt. When used in the developing solution it is converted into the normal salt by the alkaline carbonates:



There is in the market a solution sold under the name of *acid sulphite* marking 30° Baumé. It consists of bisulphite with sulphurous acid in great excess.

It is employed for keeping the solutions of pyrogallol, hydroquinone, etc., free from oxidation, and as a clearing agent in the thiosulphate fixing bath.

What is, besides preventing the oxidation of

* According to some authors the sulphates act as feeble restrainers.

the reagent by the atmospheric oxygen, the action of sodium sulphite in the development?

When in great excess it retards the development: this has been observed by all the operators. And what is important, Mr. H. Reeb has constated that the reduced silver is *black* when the image is developed by hydroquinone compounded with a small dose of sulphite, while it is white or gray-white if the dose is large.

Hence, says Mr. Reeb, sodium sulphite in great excess retards the formation of the silver deposit and whitens it.

A solution of sodium sulphite at 10 per 100 is sufficiently concentrated to dissolve silver bromide.

RESTRainers—ACCELERATORS.

As the name indicates it, the restrainers retard the development of the latent image, but does not stop it entirely unless employed in very large doses. They act, therefore, in opposition to the alkalies which increase the reductive power of certain reagents and, as

before explained, predispose the silver salts to be acted upon by the developer.

The action of the restrainers is necessarily in proportion much greater on the parts the least impressed than on the others, the high lights, for in these the silver salt having a great tendency to dissociation, the reductive action will dominate while it will be feeble on the former, that is, the half lights or details in the shadows. This explains their use in cases of over exposures and whenever it is useful to increase the contrasts in the image. Other means are at our disposal for the same purposes, but these are often of a great utility.

Various salts are employed as restrainers or regulators. Such are the alkaline haloids, NaCl, KI, KB₂, the citrates, sodium biborate (borax), the picrates, etc. The two latter are very energetic, the picrates especially.

Potassium bromide is usually employed. Its mode of action is not well know. It very probably acts by its tendency to form a double salt with *nascent* silver, KAgBr₂, upon which the developer does not act with energy. It is well known that the corresponding iodide salt is insensitive to light.

The action of the other alkaline haloids is similar.

Certain organic substances, sugar, glycerine, gelatine, etc., act also as restrainers either in virtue of their viscosity or their tendency to form feeble compounds with silver (Meldola). These substances, among which albumen should be included, are termed *physical restrainers*, to distinguish them from those, the *chemical restrainers*, which are capable of combining with silver in the nascent state.

The action of the physical restrainers is feeble, but sufficient to prevent fogging with developers compounded with the alkaline carbonates in normal doses.

With the ammonia-pyrogallol developer a restrainer, potassium bromide, is indispensable to obtain clear negatives. For normal exposure-times the proportion may be from 3 to 5 for 1000 parts of water with 5 parts of pyrogallol and from 6 to 8 parts (a large dose) of concentrated aqueous ammonia. In this formula the quantity of restrainer suffices for the purpose in question, but not to cause a marked restraining action.

The caustic alkalies KOH, NaOH, are sel-

dom employed with pyrogallol; they act too energetically with it. When used with hydroquinone and eikonogen—the latter especially—a small quantity of potassium bromide is quite advantageous to keep the shadows clear.

With the carbonates, K_2CO_3 , Na_2CO_3 , the restrainers are employed only in special circumstances and always in very small quantities; 3 for 1000 is a large dose in case of over exposure.

To resume, the restrainers are employed:

1st. *To prevent fogging by checking the too energetic action of the caustic alkalies;*

2nd. *In cases of over-exposures to prevent the image of developing rapidly in all its parts and, therefore, to allow the lights and half-lights to appear successively in keeping their relative values;*

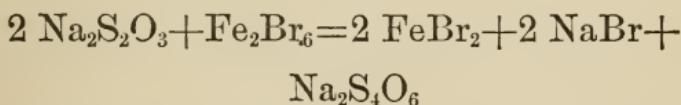
3rd. *To obtain contrasts when the subjects are greys uniform;*

4th. *To keep the lines clear when photographing engravings, pen and ink drawings, etc.*

With extra rapid plates, the restrainers are always useful to keep the shadows free from fog.

There are two compounds which effectually cause a more rapid development: sodium thiosulphate (hyposulphite) and a mixture of the same salt with mercuric chloride. The former is employed with the ferrous oxalate developer, the other with eikonogen.

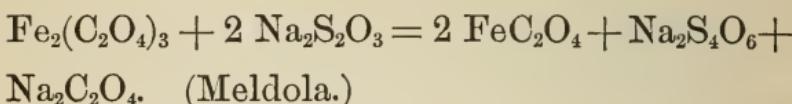
The chemical action giving rise to the acceleration, when sodium thiósulphate is added to the developing solution of ferrous oxalate consists, says Capt. Abney, who introduced this accelerator in 1880, to convert the ferric bromide formed during the reduction of the silver salt into sodium bromide whose restraining action is less energetic; thus, according to Abney:



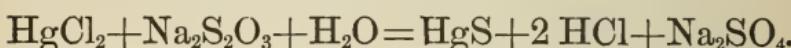
Dr. Hermann W. Vogel attributes the acceleration to the hyposulphite of iron.

In reality the cause is not well ascertained, for a much more complicated chemical change occurs: the ferric oxalate resulting from the oxidation of the ferrous salt, which acts as an enegetic restrainer, is deoxidized with formation

of sodium tetrathionate and sodium oxalate :



As to the action of the mixture of sodium thiosulphate and mercuric chloride in the eikonogen developer, we do not understand it. The mercuric salt is converted into sulphide in presence of sodium thiosulphate :



There is no thiosulphate of mercury and no sulphite.

According to Wolf and Lenhard turpentine oil acts as an accelerator with hydroquinone ; 5 or 6 drops added to 100 cubic centimeters of the developing solution suffice.

Dr. Eder states that the addition of a tincture of iodine compounded thus —

Iodine	1 part,
Alcohol	50 parts,
Water	50 "

acts in the same manner with hydroquinone. "From 3 to 6 parts added to 480 parts of the developer cause the image to appear instantaneously." "The contrasts are softened. When

the exposure is instantaneous, one obtains a weak cliché. Four parts added to an eikonogen developer have a less marked action, but the image is clearer."

In our practice we found that iodine acted as a restrainer.

SUMMARY OF THE ACTIONS OF THE CHEMICALS EMPLOYED TO COMPOUND A DEVELOPER.

Pyrogallol, hydroquinone, eikonogen and ferrous oxalate are the agents which, in a developing solution, effect the reduction of the silver salts acted on by light and, therefore, the development of the latent image. *As a consequence, they tend to produce intensity and contrasts.*

With the exception of ferrous oxalate and certain organic ferrous salts which are capable *per se* of developing the image, the reductive property of the other reagents is not generally sufficiently powerful to effect it unless the image be strongly impressed.

The reductive property of the developing solutions compounded with the reagents in question is exalted by the alkalies, the action being more effective with pyrogallol which unites to the bases forming a pyrogallate, so-called, oxidizing very rapidly.

The alkalies exert also a very important action without which the reducing influence of the reagent would not be sufficient to develop in time the weak impression formed during the period of short exposures: they act on the whole photo-film, causing the constitutive elements of the silver haloids to be easily dissociated by the developer. *Hence, they tend to produce softness and harmony, and fogging by excess.*

The sulphites having for oxygen a great affinity, prevent the oxidation of the reagents by absorption of the atmospheric oxygen, without, however, impairing their reductive property or, at least, to an extent without importance, if not employed in great excess.

Practically, the sulphites prevent yellow fog so long as the reagent is not much oxidized, when it forms a compound possessing tinctorial properties.

The restrainers act in opposition to the alkalies and necessarily more effectively on the half tints than on the high lights or parts the most strongly impressed. *Therefore, they tend to produce contrasts and to prevent fogging.*

Potassium bromide is usually employed. Its action is energetic. In a normal developer 1 per 500 is a large dose for correct exposures.

Potassium ferrocyanate is a weak restrainer. It is especially useful to obtain clear clichés when the plate should be treated with large doses of alkalies, or first treated by the same, then gradually adding pyrogallol, or other reagents. 2 per 100 is an ordinary dose.

We have, now, little to say about the applications of the reagents. They will be explained *in extenso* under the proper headings. We have, however, to call the attention of the student to the following facts which explain the various modifications made in the developing mixture to meet every case of exposure and, especially, the lighting of the subject.

A given quantity of reducing agent, pyrogallol, for example, can reduce only a certain

amount of the silver salt forming the photo-film and, as a consequence, produces a proportionate opacity, since the reduction of the silver-film commences from the surface.

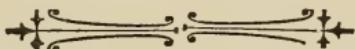
Hence, if to a solution of an alkali a small dose of pyrogallol be added, the whole silver-film being acted on, the image gradually appears in all its parts, owing to the secondary action of the alkali, without, however, assuming much intensity on account of the weakness of the reducing solution, and its action being divided all over the film.

Therefore, the parts the most impressed by the luminous influence—the high lights of the image—although first making their appearance, as it should be expected, remains weak, while the other parts—the details or half tints—develop in taking a greater intensity in relation to the former. In fact, should the exposure have been lengthened the whole image would appear at once, so to say, and remain stationary.

But if the dose of pyrogallol be increased to the maximum so as to subdue or partly annul the special action of the alkali, then the development proceeds as before, but the high lights

go on rapidly intensifying before the details appear or assume a proportionate opacity. The result is, therefore, a cliché too intense in the lights and, consequently, yielding harsh positive impressions.

On these actions is based the *modus operandi* of the development.



CHAPTER II.

THE DARK-ROOM ILLUMINATION.

We will not describe the dark room. Any arrangement is good. The main point is that the light does not impress the photo-films.

In working the wet and dry collodion plates —except, however, those prepared with silver bromide only—the light from a petroleum lamp transmitted through an orange-colored glass backed by a ground plate is safe at the distance of about one metre, but not when preparing or developing gelatine plates which are sensitive to the green rays and even to the red when they are very rapid.

Generally, glass plates stained red in the mass by copper are preferred in such a case. Most of the dry plate lanterns are made with these *ruby* plates.

Paper dyed with chrysoidine, and glass plates coated with gelatine colored with this substance may be employed as substitutes for red-stained plates. The gelatine mixture is compounded thus :

Gelatine	8 parts,
Chrysoidine	1 part,
Glycerine	1 "
Water	30 parts;

when dissolved add a warm solution of

Chrome alum	1 part,
Water	10 parts.

Coat the plate while the solution is warm. When solidified the gelatine is insoluble.

A good, red-shellac varnish or thick, plain collodion colored per cent with two parts of chrysoidine transmits also a safe red light.

Manchester brown is equally an excellent dye for the purpose in question. It transmits the red light only.

If one objects to the red light as being tiresome to the eyes, a light-red ground-glass superposed on a green one, or a combination of a ground deep orange-colored glass-plate and a yellow-green one can be used; or a ground plate coated on the back with a varnish

or collodion deeply colored with fluorescein.*

To develop orthochromatic plates a red light only is safe, and not much of it when the plates are red sensitive. According to Mr. Fred. Ives "a dark yellow-green glass is the safest light to develop by." †

It is always a good precaution to test the actinism of the light. For that purpose cover a photo-plate with an opaque material, a black cardboard more than twice longer than the plate and with an opening cut in the middle of it. Now, uncovering the opening previously placed on the lower part of the plate, expose to the light at a distance of five centimeters for, say, thirty or forty seconds; then repeat the operation by uncovering another part of the plate and exposing for the same period at a distance of one decimetre, and proceed by successively increasing the distance to two,

* Fluorescein is almost insoluble in water, soluble in alcohol, which then exhibits a beautiful, green fluorescense. The solution in ether is yellow and not fluorescent. Fluorescein absorbs all the rays of light but the yellow and red. The diluted solution gives an absorption band in the green.

† Cathedral green-glass backed with an orange-colored ground-plate.

then to four decimetres: by developing you will ascertain whether the light has on the film any actinic action or not and, if it has, at what distance from it it is safe to operate.

Many forms of lanterns have been devised for lighting the dark room. We advise the reader to select a very large one: if the light is safe, it can be used in great quantities. Carbutt's *Multum in Parvo* plate lantern is excellent and serves for several purposes.

CHAPTER III.

THE EXPOSURE-TIME.

Although the gelatine plates allow on account of the elasticity of the developing methods a certain latitude in the exposure-time, one should avoid to over expose in excess and most decidedly to under expose. Hence, when exposing by the drop shutter the largest diaphragm consistent with good definitions must be employed and the speed of the drop shutter as slow as the scene or the distance permits.

The exposure-times are classified by photographers as *normal*, *over* and *under exposures*, which latter means a *short exposure*, for a plate which has been really under exposed will never yield but a bad white and black image.

The normal exposure, as the name indicates it, is correct, or more properly speaking, sufficient. In developing, the image gradually appears, the high lights coming out first, then, and soon after, the details in the shadows, while if the plate is over exposed, the image flashes out, the details appearing almost simultaneously with the high lights, the pictures being, therefore, deficient in contrasts, without vigor if the development is not regulated. On the other hand when the exposure is short to a certain extent, the lights develop slowly, the half tints hang back, and no matter how the development is managed, the picture is seldom a good and complete one : instantaneous views, for example, unless taken with a large diaphragm to place the principal subject well in focus and more or less sacrificing the rest.

From what precedes, it follows that :

1st. *Normal exposure-time leads to obtain photographs full of details or half tones, softness or vigor being obtained at will by the development.*

2nd. *By short exposure-times greater contrasts and brilliancy are produced at the expense of the delicate details in the shadows, and if one forces*

the development to bring them out, then the half tones in the high lights will be blocked up ;

3rd. Over exposure-time produces softness and, by excess, flatness, which latter can be remedied by the development. However, the lights are generally solarized, that is, more or less devoid of half tints, and the whole picture liable to fog ;

4th. By under exposure-time—real under exposure—no good pictures can be obtained ; they are harsh, white and black.

It must not be inferred from these statements that an exact exposure-time is a *sine quâ non*. There is, on the contrary, a certain latitude, as said above, so much the greater as the plates are less sensitive ; and whenever there is not a great excess one way or the other, it is always possible to obtain negative clichés technically good.

A normal exposure-time may be defined the exposure which, with a given brand of plates developed by the following developer yields a perfect picture, provided the subject be lighted without great contrasts.

Sodium sulphite,	3.	parts,*
Sodium carbonate	2.	"
Potassium carbonate	1.	part,
Pyrogallol	0.5	"
Potassium bromide	0.01	"
Water,	120.	parts.

The normal exposure-time varies, to a certain extent, with the energy of the reductive action of the developer and its temperature.

The above definition applies only to a solution of pyrogallol at 16° C. (60° Fahr.) † compounded as in the above formula.

To study the effects of various periods of exposure, let us make the experiment following:

Subject—a spring landscape with foliages in the foreground; lighting—fair; lens—a Dar-

* We give all the formulas in parts; grains or grams for the solids; minims or cubic centimetres for the liquids.

† The influence of heat on the development was demonstrated in 1862, by Dr. John W. Draper, then president of the American Photographical Society. A dry collodion plate was treated by "hot development" and another by a developer at 40° F.; the image in the former case came out rapidly with good details, while the other slowly developed, the light being intensified before the details were visible. The relation between the temperature and the developing time is about as follows: at 10° C., 3 minutes; at 20° C., 2 minutes; at 30° C., 1 minute.

lot's rectilinear 30 centimetres focus; stop $\frac{3}{2}$; plate—a Carbutt's B sensitometre 20. We first draw the lid one-fourth off and expose 3 seconds; then, drawing the lid one-fourth more we expose 2 seconds and thus proceed exposing 2 seconds and, lastly, 1 second. The exposure-times are therefore thus graduated: 8," 5," 3," 1."

Now, nearly as soon as the plate is immersed in the above developing solution, the first fourth of the image, that corresponding to 8 seconds exposure, appears in all its details and rapidly intensifies, the whole being veiled by a superficial reduction; the second fourth will appear very soon after and give a picture deficient in contrasts, while the next fourth exposed for 3 seconds being well exposed, will develop regularly, the high lights, half lights, and details in the shadows appearing one after the other at short intervals and intensifying with their relative value. As to the part exposed only during 1 second, the high lights will appear probably not before a minute or more, and intensify much before the details are visible.

Therefore, in this example, 8 seconds is an

exaggerated over exposure-time; 5 seconds is also an over exposure-time: but, in both cases, by properly managing the development, still a fair picture can be obtained. 3 seconds is the so-called normal exposure and there will be no trouble to obtain a perfect picture if the lighting of the subject is good, as we suppose it: we have only to allow the development to proceed. The 1-second is no doubt too short an exposure, maybe not past remedy if the developer is compounded with excess of alkali, little pyrogallol, and so forth, as it will be further on explained.

The exposure-time for portraits in a photographic studio is *about* as follows:

Stop $\frac{f}{8}$,* plates sensitometre 25 c., $2\frac{1}{2}$ seconds,

" " " 23 c., $3\frac{1}{2}$ "

" " " 20 c., 5 "

[See NOTE, page 60.]

* The figures $\frac{f}{8}$, $\frac{f}{32}$, indicate the diameter of the aperture of the stops in relation to the equivalent focus of the lens, thus: $\frac{f}{4}$ means an aperture of one-fourth the focus; $\frac{f}{8}$ that of one-eighth the length of the focus, &c. Practically a lens requires *about* the same exposure-time as another of the same construction similarly stopped down, that is, in the same proportion relatively to the focal length; and, as the quantity of light passing through apertures increases or diminishes with the square of the difference between the apertures it follows

For out-door works, landscapes:

Stop $\frac{f}{32}$,	plates sensitometre 25 c.,	$1\frac{1}{2}$	seconds,
" "	"	23 c.,	$2\frac{1}{2}$ "
" "	"	20 c.,	$2\frac{1}{2}$ "
" "	"	16 c.,	$3\frac{1}{2}$ to 4 seconds.

[See NOTE.]

NOTE.—By full day-light, *i. e.*, from 10 to 3 o'clock in April, May, June, July, and August; then the exposure-time increases as the sun is lower on the horizon. For extra rapid gelatine plates, one-third less than for plates sensitometre 25 c. Lens R.R., equivalent focus 32 centimetres.

The exposure-time varies very much for landscapes, thus: the exposure being 1 second for a panoramic view, will be, say, 3 seconds with foliages in the foreground, 6 seconds and more if the foliage is dark green and badly lighted, &c.

that the exposure-time varies in the same ratio, thus: if, say, one second is the exposure-time required with $\frac{f}{4}$, it should be increased four times with $\frac{f}{8}$ which is twice a smaller aperture, sixteen seconds with $\frac{f}{16}$ which is four times smaller than $\frac{f}{4}$, sixty-four seconds with $\frac{f}{32}$, &c. However, in practice it is found that the exposure-time does not so increase, being less.

In our practice we use $\frac{f}{16}$ for rapid exposures by the drop shutter, and for landscapes $\frac{f}{22.6}$ or $\frac{f}{32}$ as the smallest stop.

For general use, Carbutt's plates sensitometre 25 are recommended.

As it has been already explained in the beginning of this work,* a very curious series of phenomena occurs during the exposure-time. It seems that the longer the exposure the more opaque should be the blacks of the cliché, that is, the parts corresponding to the whites of the model; but it is not so. After a certain period light destroys what it has done, the blacks become less intense, then more and more transparent; they are solarized. The degree of intensity obtained by the development does not, therefore, coincide with the time of isolation beyond a certain limit; and, as the action of the lights reflected from the model varies with their intensity, it should be necessary to vary the exposure-time for every one to photograph them with their real value. Of course this is practically impossible; the exposure-time is the same for all the parts of the film. How shall we proceed, then, specially if the object presents great contrasts of lights and shades, etc.? The reader has already given the answer: by prolonging

* We beg to be forgiven for sometimes repeating over what we have already explained. Repetitions are unavoidable in a work specially written for students.

the period of exposure in order to allow the weak lights of more strongly impressing the photo-film. But then an unavoidable, although less objectionable, defect occurs—the picture is more or less solarized, and the most delicate half-tints in the high lights disappear.

To a great extent this may be prevented by the manner of conducting the development and, more effectually, by the orthochromatic process.

As a rule—*When the subject is strongly illuminated and shows great contrasts of lights and shades, the exposure-time should be increased and, as a consequence, shortened when the lighting is too uniform, the subject wanting in vigor and brilliancy.*

Hence, whenever the subject is lighted by violent contrasts one should not hesitate to expose three to four times longer than the so-called normal exposure requires, for in such cases one may over expose without exposing enough, that is, without reaching that peculiar period observed by Janssen when the high lights are re-impressed.

The photo-film so impressed should be

treated by a weak and diluted developer as it is explained, with examples, in Part II.

To determinate *a priori* the correct exposure-time is the stumbling-stone for the student, in fact it depends on so many and various conditions—the actinism of the light which varies with the season, the time of the day, the color of the atmosphere often yellowish in summer and autumn, the color or ensemble of colors of the object, its distance, &c.—that even the experienced photographer can only guess it approximatively.

Many photometres have been devised for the purpose in question. That of Woodbury is good for long exposures and specially for printing by the carbon, photoglyptic and photo-engraving processes when an exposure of a few seconds more or less have but little influence on the result, if any; but, as the quality of the light is ascertained by the color of the reduction of silver chloride compared to another one printed on the apparatus, which it is not easy to judge well, it is not very reliable for exposing rapid photo-films.

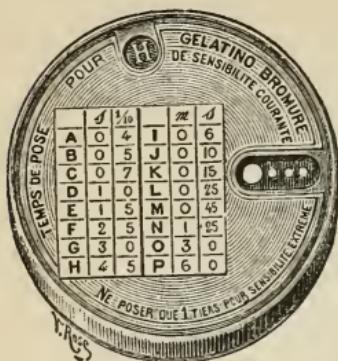


Fig. 717.



Fig. 718.

A more practical photometre is that devised by Mr. J. Ducaudun, of Paris. It is represented in the figures above. To use, after having taken the focus and placed the diaphragm, the sector, consisting of three apertures, is applied on the ground-glass, in such a manner as the largest opening corresponds to the mean lighting of the subject. Then one turns the knob placed in the centre of the apparatus until the three luminous points become almost undiscernible. Now the required exposure time will be found by the figure opposite to the letter visible in the circular aperture at the back.

These are engenious apparatus. They can render real services but can not replace the

experience one acquires by practising : nothing is mechanical in photography. If the photo-films were all of the same sensitiveness, if the subjects were all alike, of the same color and normally lighted, of course they would be invaluable : but it is not so ; the exposure-time is not only subordinate to the actinism of the light but also to all these influences, and cannot be determinated by any photometre, however perfect it is. It is therefore a study to make. The difficulties are not, however, as great as they may seem to the reader. By well-conducted experiments they soon will be mastered.

The exposure-time for gelatine plates does not exceed twenty-five to thirty seconds, except in some special cases, as photographing interiors, for example, when it may extend to several minutes.

To count seconds in the glass-house nothing is more convenient than a pendulum. A lead ball fixed at the end of a wire or a string one metre long oscillates very nearly in one second.*

* The time of oscillation for the same pendulum varies

An empirical manner of counting seconds out doors is to rapidly pronounce four syllables —*pho-to-gra-phy*, for example—which require the period of one second or thereabout. For an exposure of four seconds, these syllables should be four times repeated *without interruption*. Examples: for one second, in uncapping the lens say *pho*, &c., and cap the lens in pronouncing *pho* again; for half a second, uncap in pronouncing *pho*, then say *to-gra* and cap in pronouncing *phy*, &c.

with the height and latitudes, increasing from the equator to the poles and *vice versa*. The oscillation does not vary with the length of the pendulum, but as the square root of the length, thus: a pendulum oscillating in one second should be four times shorter to give an oscillation of one-half of one second.

To oscillate in exactly one second the length of the pendulum should be in—

London, . . .	994	m.m.	123,	Latitude	51°, 31', 08'' N.
Paris, . . .	993	"	866,	"	48 50 14 "
New York, .	993	"	168,	"	40 42 43 "
Washington,	993	"	009,	"	38 53 23 "
Rio Janeiro,	991	"	693,	"	22 55 13 S.

(Pouillet's *Éléments de Physique*, pp. 100, *et seq.*)

PART II.

THE DEVELOPMENT IN THE GELATINE
PROCESS.

FIXING, INTENSIFICATION, AND REDUCTION.

CHAPTER I.

GENERALITIES ON THE DEVELOPMENT.

The negative clichés on dry photo-films are developed by the *alkaline method*, that is, by exalting or assisting the reductive property of the reagent, pyrogallol, etc., with an alkali.

Experience shows that when the developing solution is compounded with a large dose of reagent and a quantity of alkali sufficient to cause the reduction of the silver salt modified by the agency of light, a greater intensity is obtained in the high lights of the image, which first make their appearance, the half tints hanging back for a period so much the longer as the exposure is shorter; but that if the dose of alkali is in excess, the development proceeding more regularly allows the little impressed parts of the film, that is, those corresponding to the half lights or details, to develop

before the high lights take a great intensity. In the former case, harsh, white and black images are produced ; in the latter the gradations from light to shade is preserved.

Hence, the development should be regulated according to the lighting of the model * and the exposure-time, which is shown by the more or less rapidity of the development and the appearance of the image in the first period of the same. For example : when the film is over exposed, or the model uniformly lighted, the image having a great tendency to flash out in all its parts and, therefore, to yield an image without contrasts, little alkali should be added to the developing solution, while in the opposite case, short exposure-time or lighting with great oppositions, it is necessary to increase the dose in order to bring out the half tints *in time* or, in other words, before the high lights have gained much intensity.

However, the development should never be forced. It is, on the contrary, a general rule to gradually *build up* the image, whereby the gradations are better preserved and even im-

* See our work "The Lighting in Photographic Studios."

proved. Moreover, a great excess of alkali may produce fogging just as well as an exaggerated over exposure or actinic light in the dark room. It also may cause, for the reason before explained,* a light superficial reduction of the silver salt not acted on by light before the details are fully developed, or before a sufficient intensity is obtained.

It should also be observed that the results of rapid and slow development are not exactly the same. By the former method exceedingly delicate details may be obliterated owing to the coarseness of the silver molecules;† when, by the other method, they will be well defined and quite sharp on account of the small size of these molecules. Therefore, in micro-photography, and whenever very small objects are photographed, it is advisable to develop slowly —within reasonable limits, of course.

From what precedes we can already deduct the two rules following, which are indeed

* See the action of the alkalies in the development.

† The molecules of silver bromide formed in rapid emulsions are coarser than those formed in emulsion of ordinary sensitiveness. The granulation is visible on the plates.

exceedingly important; the art of developing is based upon them.

1st. *In cases of normal and, specially, of short exposure-times, or when the model is lighted by strong oppositions of lights and shades, in order to secure gradation, the details should be first brought out, and intensity afterwards obtained by increasing the reductive power of the developer with large doses of the reagent.*

In operating otherwise, whatever be the photographic process—wet or dry collodion, gelatine process—there is much danger of burying the half-lights in the lights or, at least, to obtain high lights without penumbra.

2nd. *When the plate is over exposed, or the model uniformly lighted, the high lights should be allowed to develop before the delicate details commence to appear, always pushing to intensity.*

Let us make an example both of exposure-time according to the lighting, and of development according to the contrasts of lights and shades.

We have to photograph a church of which

the front is brightly illuminated and the side in the shade. Therefore to reproduce the shadowed side we lengthen the exposure-time more than it is necessary to photograph the brilliantly-lighted front, otherwise from want of exposure it would be impossible to develop the former.*

Now, let us suppose we develop the latent image with what is termed a *normal developer*, or, in other words, one containing a full dose of pyrogallol; then the front of the church will appear rapidly and acquire a great opacity before the parts in the shade have time to develop with a sufficient intensity: result, a bad negative.

Hence, the exposure-time is not by itself sufficient to produce a good picture. If instead of operating in this manner we modify the reducing action by compounding the developer with a small dose of pyrogallol and the same of alkali or, even better in the case in question, by increasing the proportion of the latter, then the high lights or parts of the

* We have selected this subject as being a difficult one to photograph. We could as well have taken for demonstration a model lighted *à la Rembrandt*, so called.

church strongly lighted will develop first as before, but slowly gain intensity owing to the small dose of pyrogallol, while the details or parts in the shadow will more rapidly develop from the particular action of the alkalies predisposing the feebly-impressed silver-bromide to be more easily acted on by reducing-agents, and gain a certain intensity, especially by not rocking, for reasons which are explained in the following lines : result, an ensemble very satisfactory, if not perfect.

Hence the rule :

Expose for the details in the shadows and develope to force them out and PRODUCE WEAK INTENSITIES : the high lights will take care of themselves.

Of course if the subject is wanting in contrasts, the exposure-time should be short and the development conducted in the opposite manner.

The plates are developed in a shallow tray (glass or porcelain), using enough solution to cover them. The porcelain tray of the writer is provided with a cardboard lid to exclude

the light when the development slowly proceeds or when developing orthochromatic plates sensitive to red.

When the developing solution is energetic it is well to agitate it by rocking the tray from time to time, else marblings will very likely be formed on the image.

In so doing the development is more rapid and equal on every part of the film which is successively washed by the solution at the same strength.

By diluting the developing solution and not rocking, one obtains better half tones, especially in cases of short exposure-times, for in a state of repose, the layer of liquid in direct contact with the high lights of the image soon exhausts its energy, or nearly so, the action then continuing in the half lights which increase in vigor, while the intensity remains stationary, so to say, in the blacks of the cliché.

The image need not be developed the day the plates are to be exposed. It may be postponed for a week—a month without injury. However, in a certain period the luminous

action commences to vanish. The time required for a complete evanescence is eighteen months, according to some experimenters, three years according to others;* but, whatever it may be, it is a fact that images on gelatine plates developed three or four months after exposure require a more energetic treatment and behave as if the exposure-time was short. Consequently, in a journey of a few months it is advisable to somewhat over expose if the developement should be done at home.

To ascertain when the development must be stopped, that is, when the general intensity is sufficient to yield good positives, the image should be viewed by transparency; but, the opacity of the photo-film, the weak light by which the operations should be done render the appreciation rather difficult. It is true that when wet the gelatine film being less sensitive and the brown color to it imparted by the imbibition of the developer still increasing its insensitiveness to colored light permit one to examine the image by a stronger light and

* The evanescence is more rapid with dry collodion films.

near to it; but, nevertheless, the difficulty exists.

What is a good general intensity is impossible to explain otherwise than by practical instructions. However, some data can be given to guide the student.

Generally the development should be pushed until the details in the whites of the cliché (the shadows of the image) are quite visible by transparency, and the whites when seen by reflection, veiled so that the most delicate details are not distinctly visible, the blacks being apparent on the back of the film. When the film is of the normal thickness, the general intensity is then very likely correct; but if the film is thin the development should be pushed until the whole image is visible on the back; otherwise it is probable that the intensity will not be sufficient after fixing. In operating in this manner it may happen that an excess of intensity be the result; but, as it will be seen further on, it can be more easily corrected than the opposite defect.

The reason for operating as said above is obvious since the image being formed by the reduction of the silver haloid starting from the

surface becomes imbedded in the film, and the intensity, which is a consequence of the more or less quantity of silver reduced, ceases to gain in opacity when the whole thickness of the silver haloid is converted into metal, which is seen at the back of the plate.

On the whole to ascertain whether or not the image is well developed is difficult. It requires a great experience; moreover, the thickness of the gelatine film much varies even in plates from the same make, the development when the film is thick requiring to be pushed until the whole image disappears imbedded in a veil to obtain enough intensity.

*As a rule—Develop until the high lights and half lights are visible at the back of the film, and the half tints somewhat imbedded in the deep shadows when viewing the image by reflection.**

By following this rule a sufficient general intensity will be obtained without much alter-

* Many amateur photographers do not *print* from their negatives. They will never know what is a real good negative. Indeed, the only manner to acquire experience in judging what is a normal intensity is to make the positive proofs oneself, and not otherwise.

ing the gradations which must be preserved between the local intensities.

These, termed *local* and *general intensities*, must be explained.

The negative image is formed by various opacities of reduced silver which, being the greatest in the pure whites, diminish in intensity in the half lights, etc., while the great shadows or pure blacks are represented by the bare or slightly veiled glass. Necessarily these various intensities must keep a certain relation between themselves to yield a positive image with the gradations of lights and shades of the model. These are termed *local intensities*. They should be very intense in the high lights, less so in the half lights, etc.

Here we must open a parenthesis—

To obtain positive impressions from negative clichés a sheet of paper is floated on a solution of ammonium and barium chlorides compounded with or without an organic substance—allumen is generally employed. When dry, this paper is laid for about two minutes on a bath of silver nitrate, whereby the chlorides are converted into silver chloride, which light

blackens and reduces by elimination of chlorine. Hence, for the purpose in question the silvered and dry paper is laid on a negative cliché in a printing frame and the whole exposed to the sunlight's action.

During the period of insolation the light passing through the various intensities of the silver deposit forming the negative image, reduces the silver chloride more or less rapidly and, therefore, in greater or less quantities according as it finds a more or less free passage to the silver chloride. Now, if the general intensity is deficient, that is, if the negative image is too transparent in all its parts, it is evident that the positive will be grey, without sufficient contrasts, since the light will find an easy ingress through all the various thicknesses of the silver deposit of the negative which are, so to say, nearly of equal opacity.

On the other hand, should the reduction in high lights be strong and cover the half lights, these parts, letting only a small amount of light to pass through, will cause the corresponding parts of the silver chloride to be slowly reduced, while the light easily passing

through the transparent parts (the details or half shadows) and freely through the bare parts of the glass (the deep shadows) will blacken the corresponding parts of the silver paper long before the others being sufficiently *printed*.

The result need not be told—it is obvious.

This being borne in mind by the reader we proceed.

During the development the high lights first make their appearance, then the half lights, and so forth. Now, when the delicate tints are well out, the development proper is at an end; but the lights—if the operation has been well conducted—are not sufficiently intense and a *fortiori* the half tints. Therefore, if the development were then stopped the *general intensity* would be weak and the negative cliché would never yield but a flat, weak positive image. Hence, one must necessarily let the development go on to obtain a dense enough general intensity, and as the reductive action is always greater in the parts most impressed, the gradation of the local intensities will be preserved.

However, if the development is pushed to

excess the contrasts will increase and as the half lights would generally be buried in the lights, the cliché will *print* an image without details in the lights. This defect often observed in instantaneous photographs, so-called, arise from the development being pushed so as to obtain all the details in the deep shadows, while the exposure being short they should be sacrificed.

In the next pages we will explain the *modus operandi* of the development with pyrogallol—which, of course, apply to the other reagents—for the different circumstances which may present themselves. It is based on this rule :

The development should be conducted according to the manner the image commences to appear and its character, either by increasing the reductive power of the developing solution to obtain intensity and contrasts, or by subduing or modifying its mode of action to obtain softness and harmony.

This rule obviously necessitates that the development should be slow at the beginning at least, in order to allow the operator to follow its various phases and make the modifications in time.

CHAPTER II.

THE DEVELOPMENT WITH PYROGALLOL.

Here is a gelatine bromide of silver plate of the ordinary sensitiveness. It has been exposed. Lens: a Dallmeyer rapid rectilinear 11 inches equivalent focus; diaphragm, $\frac{1}{32}$. Subject: a view in Staten Island, New York. Exposure-time: 3 seconds; it is a normal exposure as far as one can judge *a priori*.

We first prepare the following solutions to compound the developer:

A.	Sodium sulphite	.	.	.	60	parts.
	Pyrogallol	.	.	.	15	"
	Nitric acid	.	.	.	4	"
	Water, to make	.	.	.	480	"

This solution keeps well. However, we advise one not to prepare it in greater quantity than it is wanted for use in—say a week.

B.	Potassium carbonate . . .	20 parts.
	Sodium carbonate cryst.* .	40 "
	Sodium sulphite . . .	40 "
	Water, to make . . .	480 "
C.	Potassium bromide . . .	1 part,
	Water	10 parts.

These two solutions keep well. *C* is the restrainer.

To develop, equal volumes of *A* and *B* diluted with three volumes of water would be right were the exposure-time exact and every thing else equal—the intensity of the light, the color and lighting of the subject, etc.; but this we do not know with certainty, and we have to—and, indeed, we always have to feel our way, moreover, by treating the plate with the solution so compounded the half tints in the high lights would likely be blocked up before the delicate details in the shadows are developed. Therefore, we add only half a volume of pyrogallol, immerse the plate in the solution and, from time to time rocking the tray we let the action proceed until the details in the shadows are well

* Not the washing soda which is exceedingly impure and tends to produce a peculiar yellow fog.

defined when, by adding the remainder, the general intensity will be soon obtained. By this manner of operating we let the half tints develop before pushing to intensity with large doses of pyrogallol.

Now, the plate may be a little over exposed, which we will see by the half tints making their appearance soon after the high lights. In this case we at once add a few drops of *C* to check the development, adding at the same time one volume of *A*.

Presently, let us suppose that the exposure-time is very short, as it is most generally the case when exposing by the shutter; we must then not only allow or force the details to develop but prevent the high lights from gaining intensity.

To that end some authors advise to develop rapidly by treating the plate with an energetic solution to develop the whole image at once —before the high lights have time to intensify. We found that the manner of operating with pyrogallol was far from always being effective; moreover, rapid plates so treated are liable to be fogged and the development is not under absolute control, which latter we

think quite objectionable. We do not like to work blindfolded. Hence, we prefer a slow development with a dose of "patience."

It is a fact observed by every operator that, by diluting the developer and rocking in the first period of the development, then letting the action proceed without further agitating the liquid, better half tones are obtained.

We operate in this manner: we take one volume of *B*, dilute it with five volumes of water, immerse the plate in the solution, let it soak for a minute, then add half of one volume of *A* and let the action proceed; then, according as the image appears we add more pyrogallol with or without alkali, or allow the image to develope without any doctoring, or still reduce the energy of the developer by dilution—but this happens only in cases of very short exposure-times bordering to a real under exposure.

If the plate has been over exposed we operate in the opposite manner. We mix one volume of *A* with three volumes of water, let the plate soak in this for a moment and then add half a volume of *B*.

Now, it may happen, notwithstanding the excess of exposure, that certain details hang back or, which is more likely, that all the details appear simultaneously soon after the high lights. In the former case, if they do not make their appearance within thirty seconds after the lights, it is evident that more alkali should be gradually added, waiting after each addition to ascertain what is the effect produced. In the other case, if all the parts of the image appear almost at once and, therefore, without sufficient gradations, the development should be restrained by the addition of potassium bromide.

The development needs no doctoring where the image comes out gradually: the high lights first; then, one after the other, the half lights and the details in the shadows.

The rule for over exposure-time is :

To cause the high lights to gain some intensity before forcing out the details, unless the opposition be strong.

Here is a plate. We do not know how it has been exposed, what is the subject, etc.

No memorandum has been taken. How shall we proceed?

We compound the developer with equal volumes of *A* and *B*, and dilute with five volumes of water.

The image comes out regularly in graduations. We let the action go on.

The details in the shadows appear soon after the lights—over exposure; we restrain with potassium bromide and add another dose of pyrogallol.

The details long hang back—short exposure; we add more alkali and, when the details are well defined, we increase the dose of pyrogallol if it is necessary to obtain more intensity.

This manner of operating is termed *tentative development*.

As is seen by these examples the method consists to add the pyrogallol or the alkali by small doses in order that—the image developing slowly and gradually according to the contrasts—we can at any time during the operation have control of the development and, therefore, produce any effect we judge

best to *make* an image not only photographically good but also having an artistic value.

In the above instructions we have considered the development mostly in relation to the exposure-time. If we consider it according to the lighting or the oppositions the treatment is similar.* When the lighting of the subject is uniform, the development is made as in the cases of over exposures, that is, with a restrained developer.

We shall give another and last example of the development of subjects having strong contrasts of whites and blacks, which are of so frequent occurrence both in portraiture and in out door photography.

Here is a landscape : a Queen Anne cottage and trees in the foreground, a road bordering a river, mountains in the distance. This is a common subject, but quite difficult to photograph well—that is, to develop—on account of the contrast of the *white* cottage with the *dark-green* foliage; the road should not be *snowy*, the distant mountains in the

* On this subject see our work, "The Lighting of Photographic Studios."

slightly misty atmosphere of autumn not buried in the sky, etc.

We have over exposed on account of the trees and other dark objects which are there. To develop we immerse the plate into a solution of one and one-half volumes of *B* diluted with three volumes of water and, if the plate is a very rapid one, we add a few drops (not many) of *C* to prevent fogging. In this we let the plate soak for a minute; then, pouring off the solution, we add one-eighth of one volume of *A* and pour back the mixture in the tray over the plate. Now, the white house will gradually appear, but without gaining much in intensity, then the water, then the road will come out, then the mountains and, lastly, after a certain period, say three minutes, the foliage will be visible, the intensity meanwhile gaining little in the parts which first made their appearance.

When the details in the foliage are fairly out, one-quarter of one volume of *A* is added and the whole picture allowed to slowly intensify, and when every thing is well defined and apparent by viewing the picture by transparency, if the general intensity is not opaque

enough, one adds a full dose of *A* with some drops of *C* and in a short time the cliché will acquire good printing qualities.

The development of such a subject is necessarily slow. It takes from 15 to 18 minutes, and even a longer period if, for instance, it is a snow or a waterfall scenery with figures, trees, rocks, etc., as the dose of pyrogallol should be still smaller than that above advised to start the development, in order to restrain the intensification and thus effectively preserve the modelling of the whites while the details in the dark objects are hanging back. In operating otherwise, that is, by using an energetic developer, either the half tints in the whites should be satisfied to develop the objects in the dark or the latter will be a black mass without details if the development is stopped to preserve the former.

Orthochromatic plates should also be treated with a small proportion of pyrogallol to begin the development. The reason is obvious.

Local development is done by raising the temperature of those parts which require

to be forced out or intensified. The manner of doing this is simple enough; it suffices to breathe on the parts in question through a small glass tube during the development, using not too energetic a solution.

Mr. H. Fourtier operates in the opposite manner for the same purpose. He restrains the development in the parts with intensity too rapidly by touching them with a brush dipped in the following solution after washing the plate and draining, and this done proceeds as usual :

Potassium bromide	4 parts.
Potassium citrate	2 "
Water	100 "

The above constitutes a strong restrainer.

The following is a developer for line-works:

<i>A</i> ¹ .	Sodium sulphite cryst.	40 parts.
Citric acid	2 "	
Pyrogallop	8 "	
Water	480 "	

<i>B</i> ² .	Sodium carbonate	40 parts.
Potassium bromide	2 "	
Water	480 "	

Equal volumes.

We will now give a summary of the rules and afterwards describe the processes employed to fix, intensify or reduce the opacity of clichés, and then explain the development with the other reducing agents.

CHAPTER III.

SUMMARY OF THE RULES REGULATING THE EXPOSURE AND ITS DEVELOPMENT.

I. Give full exposure.

II. Over expose so much the more as the model shows greater contrasts.*

III. Under expose but little, if any, when the model is uniform. Vigor is easily obtained by the development.

* Whenever the subject is lighted by violent contrasts one should not hesitate of exposing 3, 4..... times longer than the so-called normal exposure requires for one may over expose without exposing enough, that is, without reaching that moment of the reversal, observed by Janssen, when the lights are re-impressed. But then one should commence to develop with a developer so much the weaker as the exposure has been more lengthened.

IV. Always commence slowly the development. It is most important to have it under control at the very first period of the operation in order to be able of modifying in time its action, as judged necessary by the manner the image makes its appearance.

V. With a given quantity of pyrogallol the rapidity and intensity of the reduction increase with the proportion of alkali, but beyond which, the excess of alkali causes the half tints to develop more rapidly than before.

VI. Increasing the dose of alkali corresponds to diminishing that of pyrogallol and *vice versa*.

VII. The details appear more rapidly while the high lights (blacks) slowly intensify when the developing solution contains a small quantity of pyrogallol with an excess of alkali.

VIII. By increasing the dose of pyrogallol the developer is more energetic, and the blacks rapidly intensify in proportion to their value.

IX. By diminishing the dose of alkali the result is the same, but the development proceeds more slowly.

X. When the exposure-time is normal and the subject well lighted, the plate should be treated to obtain the details and then intensified, which is easily done in this case by adding the pyrogallol in small doses at a time.

XI. When the exposure time is short, or what is the same thing as to the result, when the model is lighted by strong oppositions of lights and shades, the developing solution should be compounded with a small dose of pyrogallol and a full dose of alkali, then diluted, whereby the half tints appear gradually while the black slowly intensify. Usually there is no necessity of doctoring the developer; it suffices to let the action go on. The development is slow.

Some authors advise to develop with a concentrated solution compounded with a large dose of alkali in order to develop the image at once in all its parts, so to say; then pushing to intensity by restraining the action with

potassium bromide. The following is a formula for drop shutter exposures:

Pyrogallop	.	.	.	5.	parts.*
Potassium carbonate	.	25.	"		
Potassium bromide	.	0.25	part.		
Sodium sulphite	.	30.	parts.		
Water	.	480.	"		

We recommend the former method.

XII. In cases of over exposure-time, or when the model is lighted too uniformly, the developing solution should be compounded with a full dose of pyrogallol and its action somewhat restrained in order to push to intensity at once, or when the details are faintly visible.

XIII. The use of the restrainer, potassium bromide, is regulated according as the image appears too uniformly. No rule can be given.

* Pyrogallol should be added by degrees, else too much intensity may be obtained at first. This is the only safe method. It can happen that by operating otherwise good pictures can be obtained; but, then, the exposure is very likely sufficient, notwithstanding the plate having been exposed by the drop shutter, if the subject is lighted without great oppositions, the diaphragm large, the plate very rapid, &c.

The point to bear in mind is that a restrainer acts in opposition to the alkalies, tending to produce contrasts by retarding the development of the half tints much more in proportion than that of the lights, which latter, in reason of being strongly impressed are always acted on with sufficient energy by the reagent.

When the exposure-time is in excess, and when developing with a large dose of alkalies, it is quite advisable to add the restrainer in small quantities to the developer in order to prevent fogging and therefore, to obtain clear negative clichés.*

XIV. Develop to first obtain gradations, and then the general intensity.

XV. In case of instantaneous (short) exposures, one should conduct the development to obtain the best possible picture of the *subject* without regard to the secondary parts which, often, should be sacrificed; for, by trying, for example, to obtain all the details in the deep shadows, the half lights may be buried in the high lights and nothing but a

* See the generalities on the **R**estrainers.

harsh, white and black image will be the result.

XVI. When photographing white and black subjects (copies of engravings, etc.) the exposure-time should be short in order to avoid *solarization*; or, in other words, to obtain pure whites.*

In this case the developer should be strong and restrained. An old hydroquinone developer gives good results, the objection is its liability of producing yellow fog.

XVII. A diluted developing solution acts as a concentrated one, provided the relative proportions of the components are the same. The only difference is that the former acts more slowly.

* See Introduction.

CHAPTER IV.

FIXING.

When the image is developed and sufficiently intense, it should be thoroughly washed and fixed. This operation has for its object to eliminate from the film the unaltered silver salts, as they would blacken under the action of light and spoil the cliché.

According to Mr. A. Duttens the film can be rendered insensitive to light so as to allow one to fix the image at any time when convenient. It suffices to wash well the plate after development; then, to immerse it for five minutes in a solution of 5 parts each of potassium bromide, acetic acid, and alum, dissolved in 150 parts of water. On its removal from the solution the plate is well rinsed, then dried; or, before this,

flowed several times with methylated alcohol to hasten the desiccation.

Before fixing it is advisable to *clear* the cliché from any yellow fog, and to wash out or decompose the oxidized developer and the alkali in order to prevent the formation of a peculiar fog—greenish by reflection, light red by transparency—consisting, according to some authors, of a very thin layer of silver formed by the reduction of the thiosulphate of silver and sodium, occurring, especially, when the fixing is done in the light. According to Dr H. W. Vogel, but not very likely, it is due to traces of silver bromide retained in the film. This, or a pink general coloration can be produced at will by fixing in an old weak solution of thiosulphate bath held in a tin tray.

The clearing solution consists of

Hydrochloric acid, or

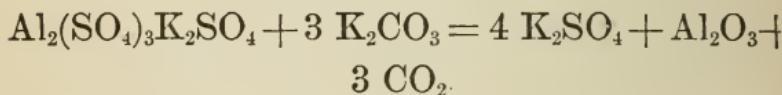
Aqua regia (6 HCl + HNO₃) . . . 2 parts.*

Water 48 "

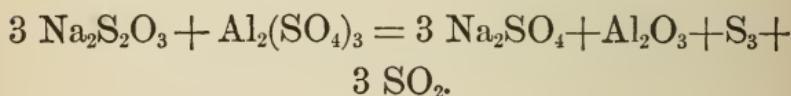
* The aqua regia should be prepared a few hours before use. It can be kept in stock in a glass-stoppered vial.

The cliché should remain for two or three minutes in the solution, then carefully rinsed before fixing.

Common alum has no action as a clearing agent either before or after fixing and is, we think, objectionable. If employed before fixing, the alkali retained in the film decomposes it with precipitation of aluminia in the film or adhering on its surface, forming yellowish-white stains—opaque by transparency:



With sodium thiosulphate, aluminium and sulphur are thrown down:



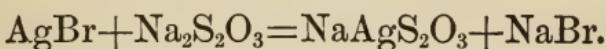
In these actions alum (double sulphate of aluminium and potassium) acts through the aluminium salt.

The latter equation shows how useless it is to add alum to the fixing bath, since being decomposed it has no action on gelatine, but liberates sulphur dioxide, SO_2 , and causes

the sulphuration of the silver forming the image.

The cliché is fixed by immersion in a solution of sodium thiosulphate (hyposulphite), the concentration of which need not exceed 20 per cent of water. In dissolving, the thiosulphate produces considerable cold, which might be utilized in the warm season to cool water; but the bath should be employed at common temperatures— 15° C. to 20° C.

In the fixing bath the unaltered silver salt is dissolved with formation of a double thiosulphate of silver and sodium.

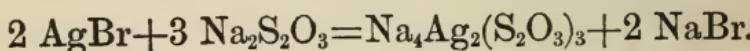


Another double salt containing two equivalents of sodium thiosulphate is formed when the fixing bath is very weak or its action almost exhausted.* It is insoluble, turns brown and then black in the light, and even in darkness.† It is also formed when the clichés

* A fixing bath containing 100 grams of sodium thiosulphate (hyposulphite) should not be used to fix more than 15 gelatine plates 15x21 centimetres.

† Silver thiosulphate is rapidly decomposed by daylight, the changes occurring even so soon as it is formed. It is, therefore, advisable to fix by a very diffused or artificial light.

—or the photographs on paper—are removed and washed before all the silver haloid is entirely dissolved :



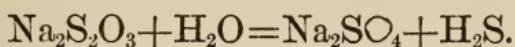
When the silver salt is dissolved, which is easily ascertained by examining the back of the plate, it is well to let the plate remain a little while longer in the fixing solution; or, as recommended for fixing photographs on paper, to place it for a few minutes in a new solution at about 10 parts of thiosulphate for 100 parts of water, in order to insure a perfect fixation.

When fixed, the film must be thoroughly washed to free it from sodium thiosulphate and consequently from the double thiosulphate, and as traces of these salts, being mechanically retained in the gelatine film, can not be eliminated by washing alone, one should have recourse to a chemical action to decompose them.

This is necessary for the following reasons :

Sodium thiosulphate in presence of dampness and the air is transformed into sodium

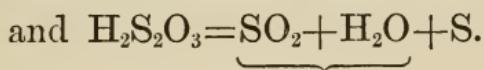
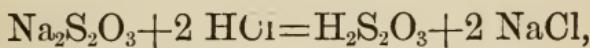
sulphate with formation of sulphureted hydrogen :



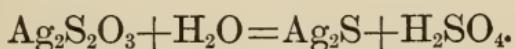
If oxygen does not intervene, sodium sulphite is formed and sulphur liberated :



All the acids, even very diluted (acid fumes in the air, for example), decompose it, evolving thiosulphuric acid which is resolved into sulphurous acid and sulphur as it forms, thus :



On the other hand, silver sodium thiosulphate splits into silver sulphide and sulphuric acid, which latter acts on the sodic salt as said above :



Now all these actions necessarily convert the metallic silver forming the photographic image into sulphide which, in time, in presence of organic matters, dampness, and other influences, undergoes certain isomeric changes producing the phenomenon known in photography under the name of fading.

The most expeditious manner of washing is to place the plates in the grooves of a small wooden tank into which the water constantly renewed enters from the bottom and runs off from above. In such an apparatus the plates are washed in one or two hours.

The complete elimination of sodium thiosulphate—but that mechanically retained in the film—is ascertained by collecting the drippings from the plate in a small quantity of a very diluted solution of silver nitrate or an aqueous solution of iodine prepared by shaking a drop of tincture of iodine in water. If any of the salt in question is present the latter solution is decolored; in the former a brown precipitate rapidly turning black is formed.

To eliminate the last traces of thiosulphate it suffices to immerse the plate for a moment in a solution of *Eau de Javelle** at 1 per 120 of

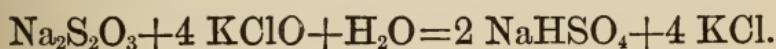
* *Eau de Javelle* is prepared by dissolving 1 part of chloride of lime (bleaching powder) in 14 parts of water, filtering, then adding a warm solution of 1.2 parts of potassium carbonate in 6 parts of water.

This compound is a mixture of hypochlorite and chloride of potassium. It acts in chemical actions through chlorine which decomposes water in setting oxygen free.

water, and then rinse the film well under the tap.

This process is due to Maxwell who recommended it in 1853 for a similar purpose in the printing-out silver-process.

The chemical action consists in converting the thiosulphate into sodium sulphate which is harmless and, being very soluble, can be washed off easily:



The following fixing solution if employed by many operators on the recommendations of Herbert B. Berkely (1883) :

Sodium thiosulphate (hyposulphite)	.	95	parts.
Sodium bisulphite, commercial, solution at 30° Baumé	.	20	"
Water	.	480	"

The advantage claimed is that the solution does not become muddy by use, clears the clichés and produces a slight intensification due to a more or less complete sulphuration of the silver. The objection is that any reduction of intensity is more difficultly effected. It is, however, a good process, preventing yellow fog either from pyrogallol, hydroquinone or eikonogen to occur in the fixing bath.

CHAPTER V.

INTENSIFICATION.

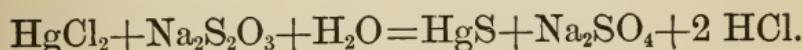
Weak negatives can be intensified in many ways. The process based on the chemical changes taking place when mercurous chloride (calomel) is treated by ammonia or sodium thiosulphate (hyposulphite) is the most employed.

It was devised by Scott Archer who, if he was not the first to use collodion as a medium to hold the silver haloids, has nevertheless the very great merit of having given us a good, practical process, so perfect that it has not been improved.

We will first give a succinct description of the chemical actions occurring in the intensification of negatives, then explain the *modus operandi*.

Mercuric chloride (*bichloride of mercury, corrosive sublimate*) occurs crystallized in colorless rhombic needles without water of crystallization. Its taste is styptic, its reaction acid. It dissolves in 15 parts of water at 10° C., in two and one-half parts of alcohol, and four parts of ether. It is very toxic. At the dose of from 3 to 5 grains it causes death. Albumen is the best antidote. In moist air and under the influence of light it is slowly decomposed into mercurous chloride; oxygen is given off and hydrochloric acid formed.

Sodium thiosulphate converts it into sulphide :



Ammonia throws down a white precipitate consisting of mercurammonium chloride :

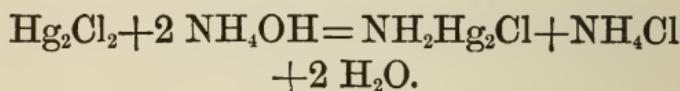


Silver immersed in a solution of mercuric chloride first blackens, then, in a certain period, a grayish-white deposit of mercurous chloride is formed on its surface :

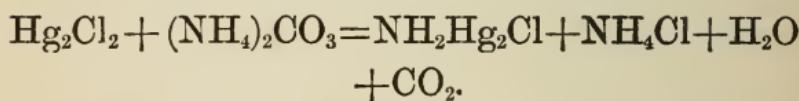


Mercurous chloride (calomel) is an insoluble white substance without taste and odor. In the light it turns yellow, then grey from a partial decomposition into mercury and mercuric chloride. Ammonium nitrate dissolves it. It is not poisonous.

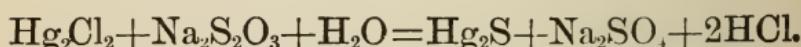
Treated by ammonia it is transformed into a black insoluble compound, mercurous ammonium chloride :



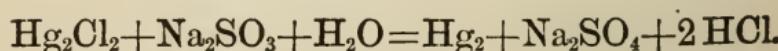
Ammonium carbonate gives rise to a similar action :



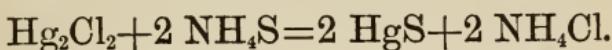
Sodium thiosulphate converts it into a black substance, Hg_2S , soluble in aque regia and resolved by heat into mercuric sulphide and mercury :



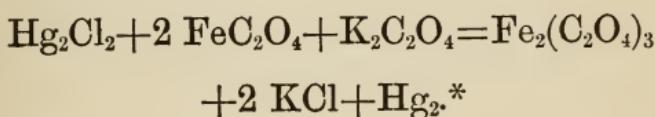
Sodium sulphite precipitates mercury :



Ammonium sulph-hydrate (ammonium sulphide) converts it into mercuric sulphide :



Treated by potassium ferrous oxalate it is reduced to metal :



The clichés are intensified when fixed and dry. They should be free from yellow fog and especially from all traces of sodium thiosulphate which by reacting with mercuric chloride stain the film brown. When this happens, the cliché must be treated by a very diluted solution of ammonium sulph-hydrate to convert the silver forming the image into silver sulphide. This done, the film should be thoroughly washed. As a certain amount of intensification results from this treatment it should be taken into account. Another essential precaution is to immerse the cliché in water for a few minutes before intensifying in

* See my paper on "The Chemistry of Mercury and its Salts, and Their Behavior in Photography," in Anthony's Phot. Bull., Vol. XX, pp. 620 *et seq.*

order to soften the film and, after the treatment by mercuric chloride, to well wash off this salt, for, as said above, it forms with ammonia a white insoluble precipitate which would be retained in the film.

Various degrees of intensification can be obtained by the mercury process and, in fact, by any other one. To that end, the chemical actions being rapid, one should operate with weak solutions, say 2 or 3 of mercuric chloride for 100 parts of water.

On the application of mercuric chloride the image first blackens from the formation of mercury oxide and, under, the amalgamation of the silver. If the action be then stopped, the film washed, then treated by a very diluted solution of ammonia or of ammonium carbonate—we prefer the latter—the minimum of intensification is obtained.

But if the action is allowed to go on, one observes by examining the cliché from the back that the half tints, being formed by a thin layer of metallic silver, are first bleached through from formation of mercurous chloride, while the high lights are only partly acted on,

that is, superficially covered by a deposit of the same, Hg_2Cl_2 . Therefore if the chemical action is stopped at this second stage the intensification will be greater in the half tints than in the high lights when the film is treated by ammonia or any other reagent. But were the whole silver converted into silver chloride, then the layer of mercurous chloride being greater in the high lights, the intensity of the latter would be in proportion more opaque than in the half tints and the contrasts of the image would necessarily be increased.

The operation should, therefore, be conducted according as whether it is necessary to increase the general intensity or the oppositions between the local intensities.

When the image is uniformly bleached through, it is still possible to modify the intensification. It suffices to employ a dilute solution of the reagent which, by acting gradually, produces the necessary change in the parts where the mercurous chloride is in a thinner layer—the half tints—before acting through the whole mass formed in the high lights. It must be admitted that the latter action is not very well under control.

Sodium thiosulphate, 5:100, is seldom selected, if ever, to blacken the mercurous chloride on account of the prolonged washing required to eliminate it from gelatine films. If employed it should be in very diluted solution in order not to dissolve the silver chloride, and thereby to lessen the opacity.*

A weak solution of aqueous ammonia is generally preferred.†

Aqueous ammonia, 26° Baumé 5 parts.

Water 100 "

or—

Sesquicarbonate of ammonium 10 parts.

Water 100 "

The intensification by sodium sulphite, 3:100, is not very opaque and allows a rapid printing. If the sulphite solution is almost

* See Professor Ad. Martin's process.

† Some authors state that the silver chloride mixed with the mercurous chloride is dissolved by ammonia. It is true that aqueous ammonia dissolves AgCl, but at the concentration it is here employed the solution is too feeble for that purpose, very little if any is dissolved.

Other authors recommend to dissolve AgCl, stating that it will blacken under the influence of light. That is an error. Silver chloride intimately united to calomel is insensitive to light.

saturated by the silver salt the intensity is much increased.

The intensification by the above reagents is rapid. That with a ferrous oxalate developer acting gradually on the mercurous and silver chloride which it reduces to the metallic state is, therefore, better under control. The *modus operandi* suggests itself. It is a redevelopment, so to speak, and succeeds well if the plate is allowed to dry before proceeding, otherwise the intensification would very likely be irregular.

The oxalate solution can be compounded as follows:

Saturated solution of potassium oxalate	30 parts,
" . . " ferrous sulphate	5 "
Tartaric acid	1 part,
Water	20 parts.
	No bromide.

This excellent process, due to Mr. A. Chardon, bears a strong resemblance with that devised years ago by Thomas Sutton for intensifying with an alkaline pyrogallol developer the clichés on collodion bleached by mercuric chloride. In fact, all the developers for dry plates can be employed in weak solutions

provided, as previously said, the cliché treated by the mercuric salt or any other agent be allowed to dry before being intensified.

When the image is weak and veiled, yielding prints without vigor, contrasts are obtained by treating it after fixing and rinsing with a solution of—

Ammonium sulphocyanate	10 parts.
Gold terchloride, 1:100,	10 "
Water	100 "

When the desired effect is produced it suffices to wash thoroughly.

For white and black images (copies of pen and ink drawings, engravings, etc.*) the following methods should be employed to obtain opaque intensities :

Carey Lee's Process. The negative is fixed, carefully washed and then treated by an iodine solution† until the films become yellow. The

* The plates we recommend for copying such subjects are "Carbutt's Process Plates." None surpasses them. However, clichés on collodion are preferable for photo-engraving.

† Iodine 2, potassium iodide 5, water 480.

plate is afterwards washed and flowed with the following solution:

Crystals of Schipp's salt (sulphantimonate of sodium)	1 part,
Water	12 parts.

or—

Filtered solution of the salt	1 part,
Water	8 parts.

Under this treatment the reduction assumes shades varying from russet to scarlet according as the yellowness of the cliché is more or less pronounced.

The Schipp's solution gradually decomposes. By adding to it a little liquid ammonia (about $1\frac{1}{2}$ p. 100) it keeps well.

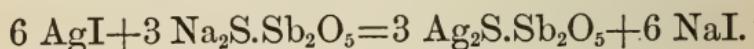
Preparation of the salt :

Grey sulphide of antimony	22 parts.
Sodium carbonate cryst.	44 "
Well burnt lime	17 "
Flowers of sulphur	4 "
Water	48 "

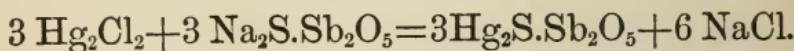
The lime is first slaked in the water and 140 parts more of water is added together with the other ingredients. Boil until the sulphide has become white, filter and crystallize. It is, however, unnecessary to take the trouble of

crystallizing as the solution can be used as said above.

The chemical changes consists in the transformation of the silver iodide into silver sulphantimonate, thus :



If the cliché is bleached by mercuric chloride instead of iodine, the intensity is greater from formation of mercurous and argentic sulphantimonates. Mercurous sulphantimonate is orange and, as in the iodine process, the argentic salt is brownish-black, turning brown as it dries. The changes with mercurous chloride are as follows :



H. Selle's Process. Prepare a solution of sulphate of uranium and another of potassium ferricyanate, both of the same strength, about 1 : 10. Mix them by equal volumes in such a quantity as may be required for one or two days' use, and pour the mixture on the fixed and well washed cliché : the silver is transformed into ferrocyanate and a brown precipitate of uranium ferrocyanate is deposited.

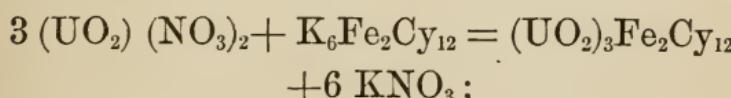
The intensification proceeds as long as necessary, and this without sensibly increasing the deposit, thus securing delicacy of details.

Instead of mixing the two salts, as recommended by Mr. Selle, it is best to first treat the negative with the uranium solution at 1 per 100, then to add to it a few drops of the ferricyanate solution, 3 : 100, and pour back the whole on the cliché until the desired effect is produced.

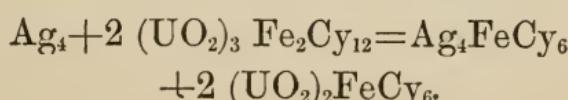
Clichés intensified by this process become more and more intense in the light and worthless if the image is in half tones. By heating them over an alcohol lamp the opacity can be somewhat reduced.

The following equations show that it is a *sine quâ non* to use *uranic* salts, sulphate or nitrate of uranyl.

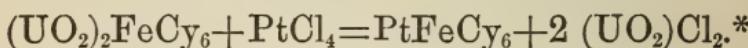
By mixing the ferricyanate and the uranic salt, uranic ferricyanate is formed :



then this salt produces the changes in question :



By treating the cliché thus intensified with aluminum chloride, 1:10, the color turns to an olive brown. With gold tetrachloride it is changed into a violet or emerald green, and black or olive-black by platinum tetrachloride:



These chemical actions are often employed to tone diapositives, etc.

Dr. J. M. Eder's Process. After treating the cliché by mercuric chloride and washing, it is immersed in a solution of—

Potassium cyanide, pure	2 parts,
Potassium iodide	1 part,
Mercuric chloride	1 "
Water	420 parts.

In this the cliché first turns yellow, then gradually to coffee-color, and then to chocolate-brown. At this stage the color commences to lighten, assuming various tints without losing any details, and the cliché becomes more transparent. If the action does not reach the brown color more cyanide should be added.

* See our papers on the Chemistry of the Salts employed in Photography in Anthony's Phot. Bull., Vols. XX and XXI.

Generally the intensifying is stopped at some of the stages of the reversal of the action, that is, when the color lightens.

The same solution can be employed to reduce the intensity of clichés, leaving out the previous treatment with mercuric chloride. The action is slow and regular.*

Intensification with silver. Although the intensification with silver is the most rational and the clichés intensified by mercury liable to fade, and those strengthened by uranium to intensify by exposure to light, we do not advise it. It is, on the whole, a risky operation, liable to stain the cliché even when every trace of sodium thiosulphate is eliminated.

To insensify by this process the cliché is immersed in water to soften the film, then for a moment in a solution of citric acid at 2 per 100, then placed until the proper intensity is obtained in one of the following developers to which have been added a few drops of a 5 per 100 solution of silver nitrate :

* The intensification is due to the formation of Hg_2I_2 whose color varies as the action proceeds and this salt is gradually dissolved by potassium cyanide when the first reaction is complete.

1.	Gallic acid	1. part,
	Acetic acid No. 8 . .	5. parts.
	Water	100. "

or—

2.	Hydroquinone	2. parts,
	Water	100. "
	Nitric acid	0.1 part.

After this treatment the cliché should be washed, fixed, &c.

CHAPTER VI.

REDUCTION OF INTENSITY.

The clichés can be too intense from three causes, viz.: 1st, Yellow fog; 2nd, General intensity too opaque; 3rd, The high lights too intense from short exposure-time or the development not having been well conducted.

1st.—Yellow fog is prevented by immersing the cliché before fixing in a “clearing solution” consisting of—

Hydrochloric acid	1 part,
Water	20 parts.

or—

Citric acid	2 parts.
Water	20 “

Mr. B. J. Edwards advises to change the yellow color of the fixed cliché into one permitting to print more rapidly. For that

purpose he places the cliché for a few minutes in a solution of—

Alum	1 part,*
Citric acid	1 "
Ferrous sulphate	3 parts.
Water	20 "

By treating the cliché after fixing and washing with the following compound, the yellow color is changed into one of steel grey :

Oxalic acid	1 part,
Water	30 parts.

According to Mr. A. Chardon, yellow and green fogs are removed without any alteration in the intensities of the clichés by a neutral or, more effectually, a slightly alkaline solution of ammonium citrate 1:50.

2nd.—The three processes following are usually employed to *reduce the intensity of a cliché in which the general intensity is too opaque*. They are known as the Spiller, Monckhoven, and Farmer's processes. We prefer the former

* Alum is not useful to remove yellow fog. We discard it unless the acid solution produces blisters, etc. See "Causes of Failures."

because no sodium thiosulphate being employed, the after-washing is more easily and effectually done, and no injurious compound is left in the film.

Spiller's Process. "The process which I now proceed to describe," says Professor John Spiller, "answers perfectly, for it can be held completely under control, be made to reduce the image at any required rate, working regularly and uniformly without any mottling and, at the same time, hardening the film so that it can be rubbed with the hand to assist the removal of any surface stains, and never once have I observed any trace of frilling.

Stock Solution A is made up of—

Alum	1 part,
Copper sulphate . . .	1 "
Common salt	2 parts.
Water	10 "

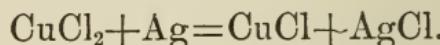
Dissolve together and filter.

Solution B is a cold saturated solution of common salt, filtered.

"For ordinary use, mix *A* and *B* in equal volumes, and immerse the negative therein. In obstinate cases, employ more of the copper

solution. When the required degree of reduction is attained, rinse with fresh salt brine and wash well with water to remove all the soluble salts.

"The chemical action is practically the attack of metallic silver with cupric chloride to form a double argentic and cuprous chloride, which is soluble in salt brine, the alum being added only for the purpose of hardening the gelatine film, thus :



"Changes of color will be observed; but watch well the altered intensity, and stop as soon as the desired stage has been reached. Always wash well in the salt brine to remove the copper, and finish under the tap, or in a few changes of water.

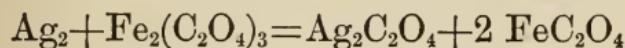
"A chemist will understand that a mixture of blue vitriol and common salt is equivalent to cupric chloride and sulphate of soda, as denoted by the change of color from blue to green when making up the solution, and in cold weather some of the sulphate of soda usually crystallizes out." *

* Year book, 1884, p. 67, *et seq.*

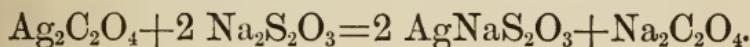
*Dr. Monckoven's Process (1882).**

Potassium ferric oxalate	15 to 20 parts.
Sodium thiosulphate	60 "
Water	480 "

In this process the reduction is effected by sodium thiosulphate dissolving the silver oxalate formed :



then—



Wm. Willis, the inventor of the platinotype, has utilized the former action, that is, the transformation of silver into oxalate, to the intensification of negative clichés by treating the bleached image, $\text{Ag}_2\text{C}_2\text{O}_4$, by a ferrous oxalate or an alkaline pyrogallol developer (1882).

Mr. E. Howard Farmer's Process. " Prepare a solution of ferricyanate of potassium by

* This process is often recommended to clear the lines in white and black negative clichés. We prefer a simple wash with an alcoholized solution of potassium cyanide chemically pure, if possible, on account of the great quantity of carbonate the commercial article contains.

dissolving one part of the salt in sixteen parts of water. To reduce the intensity immerse for a few minutes the negative in a solution of sodium thiosulphate 1:16, and then add to this a few drops of the ferricyanate solution. A gradual reduction will take place without change of color, the rapidity depending on the quantity of ferricyanate added. When sufficiently reduced, wash well the negative.

"To reduce locally, immerse the plate in water for a few minutes and apply the mixed solution with a camel-hair brush or pellet of cotton-wool to the parts required; there is no fear of markings.

"To remove silver stains, etc., on the negative, immerse it in water, rub over with a pellet of wool which has been dipped in the solution, and rinse under the tap before the solution has time to diffuse into the film.

"The solution is also efficacious with over dense silver prints." *

By this process the cliché can be reduced just after fixing and rinsing. When the cliché is a portrait which should be retouched it is

* Year book, 1884, p. 59, *et seq.*

advisable to harden the film by immersing the plate for a moment in a solution of borax at 6 per 100 of water.*

The *rationale* of this process is very simple: the ferricyanate transforms the metallic silver into ferrocyanate soluble in sodium thiosulphate:



The mixture of the two salts does not keep. The following solutions can be prepared beforehand and mixed by equal volumes for use.

A. Potassium ferricyanate 1 part,
Water 240 parts.

B. Sodium thiosulphate 40 parts.
Water 240 “

In these processes the intensity is reduced by dissolving the metallic silver forming the image. Employed to lighten good clichés over developed, that is, whose intensity is too opaque in all the parts of the picture, the relative value of the local intensities is little altered provided the operation be conducted

* Borax can replace alum to harden the film in most cases.

with great care. Otherwise it may happen—and, indeed, this is of frequent occurrence—that the half tints, being formed by thin layers of metal, do not stand the dissolving action and are washed off, thus impairing the beauty of the image past remedy.

A more rational and safe method would be to change the color of the cliché, or to render the reduction more transparent, so that the only desired change would be produced, but if the intensity was too much reduced it would always be possible to strengthen it again by an exceedingly weak developer well restrained.

For example : The cliché previously soaked in water is immersed for a certain period in an aqueous solution of bromine to partly transform the metallic silver into bromide. Under this treatment the image seems to intensify on account of the opaque yellowish-white silver bromide formed, but when exposed for a certain period to sunshine it becomes more transparent from the reduction of the silver salt which turns to a bluish violet-black.

The operation should be made by diffused light and the cliché not exposed to the sun's light until quite dry, otherwise the silver

bromide reduction would be of unequal intensity and lighter in the parts drying first. In fact, when the cliché is exposed to the luminous action under water and in presence of an absorbent of the haloid the reduction is always much darker.

If the cliché be thoroughly bleached, it is necessarily much weakened, too much so, generally; but various remedies are at hand. It may be intensified *after insolution* by a weak alkaline developer, by mercuric chloride, palladiochloride, etc.

Similar results are obtained in treating the image with a weak solution of ferric chloride very little acidified with citric acid. When the desired effect is produced, the cliché should be rinsed in a 2:100 solution of citric acid, then washed to eliminate all traces of the iron salts before proceeding.

No fixing is required after any one of these treatments; it suffices to well wash in the ordinary way.

If the cliché is too intense in the lights, yielding harsh positive impression, as it happens when the development is badly conducted, or pushed to obtain

the details in case of manifest short exposure-times, or when the developer contains too great a quantity of bromide, the image should be transformed into silver chloride or bromide, then after washing, treated by a weak ferrous oxalate, pyrogallol or hydroquinone developer, taking care to stop the development before the layer of the haloid salt in the high lights be reduced through, whereby, after fixing, the cliché will present less contrasts than before this treatment.

The solutions to transform the silver into chloride or bromide are the following:

A.	Ferric chloride	10 parts
	Hydrochloric acid	5 "
	Water	480 "

or—

B.	Iron bromide	10 parts.
	Nitric acid	5 "
	Water	480 "

Clichés intensified with mercury are reduced by potassium cyanide:

Potassium cyanide, C. P.	5 parts.
Water	120 "
Alcohol	30 "

Some operators employ this solution to reduce the general intensity.

CHAPTER VII.

CAUSES OF FAILURES.

I. *Fogging or a reduction of silver over the whole film veiling the image.*—It may occur from developing over exposed plates with a developer strong in alkali and not restrained; or, from pushing the development by over doses of the same; or, by prolonged development with concentrated developing solutions, and from the bad quality (actinism) of the light in the dark room.

For plates which fog from a bad preparation of the emulsion there is a “certain cure,” which consists of immersing the plate in a two per cent solution of potassium bichromate for about an hour and then washing out the bichromate with extreme care. “The sensitiveness after this treatment is not much

diminished, and the negatives taken with (the plates) are beautifully bright."*

Plates, gelatine or dry collodion, having been accidentally struck by light, or exposed in the camera, can be treated in a similar manner to destroy the luminous impression, and then yield good results although the sensitiveness is to a certain extent impaired. The process consists to immerse the plate in the following solution for a period of from 10 to 15 minutes; then, after a thorough washing, to let them dry spontaneously in taking the usual care

Potassium bichromate . . .	3 parts.
Hydrobromic acid . . .	10 "
Water	480 "

The sensitiveness of the plates so treated can be exalted by immersing them for a minute in a weak solution of hydroquinone, drying, &c.

II. *Frilling and blistering.*—Too much alkali in the developing solution, especially when employing the caustic alkalies; fixing solution too concentrated; long washing—tepid water softens the gelatine and causes it to swell, and as the support is rigid the film blisters and

* Abney.

tends to detatch itself from the plate, hence the defect.

If it occurs during the development it is prevented by soaking the plate before developing in a solution of Epson salt, 1:8, for a minute, and rinsing. Coating the gelatine film with plain collodion is an effective remedy recommended by Captain Abney.

The defects are now seldom met with. However, it is well during the warm season to use cold water, 15°-20° C., and to insolubilize the film after developing by immersing the plate for a few minutes in a solution of borax or of chrome alum. Edging the film with wax dissolved in benzine or with tallow before developing is a good preventative for the edges.

The solutions of acids (hydrochloric, sulphuric, etc.) employed to destroy yellow fog, or for other purposes, have a tendency to produce blisters and frilling. This is avoided by adding chrome alum to these solutions, about 5 per 100, the alum exerting a tanning action also useful to prevent by time the decomposition of gelatine (mouldiness) by the germs from the air growing in presence of moisture and organic matters

III. *Flatness.*—Normal exposure: The development was conducted to obtain the details as it is proper, but without afterwards pushing to intensity. Over exposure: The development has not been conducted to obtain intensity before or simultaneously with the details.

IV. *Negatives wanting in details.*—Developing solution too strong and rapidly intensifying.

Pushing to intensity when the details are not sufficiently developed.

Real under exposure.

V. *Negatives weak, details good.*—The development stopped before the general intensity is obtained.

The negatives can be intensified by the mercuric process.

VI. *Negatives generally too intense.*—Over development.*

VII. *Negatives strong and yielding harsh, white and black impressions.*—The development pushed to obtain the details in the shadows

* See the reducing processes.

when—the exposure being very short—they should have been sacrificed to preserve the gradations in the lights, etc.

The development conducted with too much pyrogallol to begin with.

VIII. *The image develops slowly and with abnormal contrasts, although the exposure-time is correct.*—This defect occurs when using the same developing solution over again.

No doubt the reductive power of developing solutions is not exhausted by a single operation and that several plates can be successively developed in the same solution. But whether the results are equally as good or similar is a question, for each operation not only lessens the reductive power but also originates a restraining action due to a certain quantity of an alkaline bromide formed by the reduction of the corresponding silver salt. Hence a longer exposure is required, and it does not even counteract the restraining action and compensate for the want of energy of the developer which acts more and more slowly, the contrasts increasing and the image finally refusing to develop, except in the high lights.

The addition of more alkali and of the reagent does not satisfactorily remedy these defects.

A developer should be used to develop, I will not say only one cliché, but no more than three and this in large solutions and when the same results are desirable.

For portraits a new solution is recommended.

For drop-shutter exposures it is imperative.

We have demonstrated in the preceeding pages that the tentative method of developing is the only one rational; we strongly advise the reader to adhere to it in every case.

IX. *Solarization*.—See “Exposure-Time” and “Introduction.”

X. *Halation, Irradiation, Blurring*.—A halo or blurring at the edges of the lights (blacks) and extending in the shadows and sometimes in the half lights—often seen around the branches and upper parts of trees in landscapes, the roofs of buildings, the windows in parlors, etc.—occurs whenever a bright light is in opposition to shadows or, white to black.

The cause of this phenomenon arises from the light being upwardly reflected by the back

of the glass plate. It is so much more apparent as the exposure-time is lengthened. Diffraction is also a cause of irradiation.*

The reflection is prevented by backing the plate with a substance capable of absorbing the light such as the following, which is similar to *Gihon's opaque*, used for stopping skies, etc.:

Burnt sienna, powdered	16 parts.
Dextrine	4 "
Glycerine	2 to 3 "
Water	quantity sufficient.

These ingredients should be ground together into a thick paste.

This backing should, of course, be wiped off before developing.

An excellent protection against halation is the coloring of the photo-film as first devised by Mr. Carey Lea, who advises coralline for that purpose as not impairing the sensitiveness.

"The result is obtained," said Mr. Lea,† "in a simple manner. It is only necessary to add

* On the causes of halation see Abney's communication in London, Edinburgh, and Dublin Philos. Mag., May, January, 1875; Cornu's communication in Bull. Soc. Franc. Photo, 1890, pp. 68, 160, 173; Davanne "Photographic," Vol. I., p. 165, Paris, 1886, Gauthier-Villars.

† "Manual of Photography," 2nd edition, new issue, p. 4 of the 2nd supplement.

the alcoholic solution of coralline to the finished emulsion and to employ it as usual.* Neither is there any necessity of special means of removing the color of the plate; this I would consider a fatal objection. Coralline has the inestimable advantage that it disappears by itself in the operations of developing, fixing, and washing."

"The best scarlet coralline (the yellow coralline sometimes called *aurine* is entirely unsuitable) is to be dissolved in alcohol 48 grains to the ounce. The solution takes place rather slowly and several days should be allowed with occasional shaking, neither is it ever entirely complete, a small amount of dark residue always remains, even after standing for months. To each ounce of finished emulsion from 6 to 10 minims of the coralline solution is to be added and well shaken. The emulsion is then ready for immediate use. It will not have the strong red color of corraline, but a buff or salmon shade."

* The dyed emulsion is sensitive to yellow and orange. It is employed in orthochromo-photography. Instead of adding coralline to the emulsion—collodion or gelatine—which is not a *sine quâ non*, the plate may be dyed in the usual manner.

It is advisable to always back the plates when working outdoors and photographing interiors.

XI. *Transparent spots; pin-holes.*—Bubbles of air adhering on the film during the development ; plates not dusted before placing them in the holder, etc.

XII. *Yellow stains.*—The developer much oxidized. Long development with not enough sulphite or a bad sample of it. This salt is converted into sulphate in contact with the air and consequently becomes useless. Yellow stains are promoted by hardening the gelatine film with alum before fixing. They are prevented or removed by the clearing solutions.*

When they are persistent—which happens when the cliché is fixed—the plate may be treated by a solution of *Eau de Javelle* or of bleaching powder ; or, after a thorough washing, by a diluted solution of aqua regia, 1 : 12, as recommended by Prof. Arthur H. Elliott.†

* For formulas see “Reduction of Intensity,” Part II, Chap. VI, of this work.

† Aqua regia is prepared “by mixing six volumes of hydrochloric acid with one volume of nitric acid and keeping the solution for several days in a warm place.” See Anthony’s Phot. Bull., Vol. XXI, p. 98.

We found 1:12 a strong solution. It soon disorganizes the gelatine.

Yellow fog often occurs in the fixing bath, especially when hydroquinone is used for developing. The remedy is given in the following pages.

XIII. *Crystallizations, Efflorescence on the film.*—The sodium thiosulphate not well washed out after fixing.

XIV. *Yellowish stains on the film, adherent on the film, and sometimes embedded.*—They result from not well washing the developed image before hardening the film with alum, the carbonate or the alkali forming a precipitate of aluminia, insoluble.* The defect may also be due to the chemical action occurring when sodium thiosulphate is in presence of alum. As a remedy wash the film with acetic acid and rinse well.

A good substitute is chrome alum free from acid.

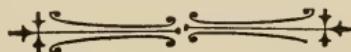
XV. *Yellow-brown stains formed when intensifying.*—The thiosulphate not entirely elim-

* By compounding the alum bath with hydrochloric acid, the defect in question is avoided. Reason, obvious.

inated by washing, or by a chemical action, reacting with mercuric chloride.*

Mr. H. E. Gunther states that stains from mercuric intensification are removed by ammonium sulphide. The plate is for a short time placed into water, "then sulphhydrate of ammonium (diluted) is poured on the plate, which is done best in the open air, as the liquid is a most ill-scented one. As soon as this has been done, the negative will at once be restored in its original clearness. Finally, the plate must be thoroughly rinsed and washed."

* See "Fixing," Part II, Chap. IV,



CHAPTER VIII.

THE DEVELOPMENT WITH HYDROQUINONE.

Hydroquinone does not possess the superior and extraordinary qualities which have been attributed to it.

The reductive action of pyrogallol is more energetic than that of hydroquinone, the latter requiring to be employed in larger proportions and to be compounded with greater doses of alkaline carbonates, or with caustic alkalies, KOH, NaOH, to increase the reductive action.

It does not allow more latitude in the exposure-time than any other reagent; and, what is more important, it does not possess the elasticity of pyrogallol, and the modifications during the development, which one thinks necessary to make in the constitution of the developer to produce certain effects, do not much alter its mode of action.

The best authors recommend pyrogallol for this reason: it can be made to work in many ways and exactly as you please to obtain any desired result.

The great favor which hydroquinone finds among amateur photographers is due to the facility with which it can be used, and to its remarkable keeping quality when compounded with sodium sulphite, which permits one to prepare ready-made solutions in which a number of images can be developed one after another in a sort of mechanical manner, so that photography has become nothing but a toy in the hands of many would-be amateurs. They may—in their ignorance of the theory of the process, the action of each chemical, the changes constantly taking place in the developer—occasionally produce very fine photographs, but they generally obtain indifferent or bad ones: *Rien de bien ne se fait au hazard.*

It has just been said that the solution of hydroquinone and sodium sulphite possesses very good keeping qualities; but if it remains colorless it nevertheless undergoes in a certain period a marked change in its developing power. Mr. Londe has ascertained by a series

of experiments that the alteration is quite apparent after five days keeping.

As pyrogallol and eikonogen, hydroquinone produces yellow fog* by long development when the developer is oxidized to a certain extent. It must be admitted, however, that the yellow coloration can be easily avoided and that in ordinary circumstances it yields very clear clichés, which is certainly a very great quality for the reproduction of engravings, etc., and for transparencies, but which for half tone, negatives may become objectionable, for a slight veil all over the cliché is generally useful to prevent harshness.

No doubt hydroquinone is an excellent developer capable of rendering good services if properly managed and when employed for the development of such subjects as those which have been alluded to. It is, for example, the best agent to be used for diapositives and duplicate negatives. The color of the reduced silver is fine and all that can be desired for lantern slides and ornamental transparencies.

From the foregoing criticisms we do not

* An old solution of hydroquinone is exceedingly liable to produce deep yellow fog.

mean to say that good negatives cannot be regularly obtained with hydroquinone, but simply that the development cannot be so well regulated as with pyrogallol, which we consider the developer par excellence.

The development with hydroquinone is conducted according to the principles which rule the development with pyrogallol.

Generally, it is advisable to commence developing with a solution having but a medium reductive energy.

It is advisable to add some bromide to the developer at the very beginning of the operation, although it may be left out with certain brands of plates. Added in small quantities this restrainer exerts no prejudicial action on the details of the shadows, but helps to keep the cliché clear, especially if the plate has been fully exposed.

Sodium sulphite has a marked influence on the development with hydroquinone—the greater the dose the stronger the contrasts and *vice versa*.

By diminishing the proportion of hydroquinone less density is obtained, also by using

large doses of the alkalies, but then with the usual results.

In case of a short exposure-time bordering to under exposure, the development with hydroquinone can be lengthened more than with the other reagents, which is a great boon to obtain what can be had of the delicate details in the great shadows. The developing solutions should be diluted.

To develop prepare—

A.	Sodium sulphite, cryst.	50.	parts,
	Hydroquinone, powdered	10.	"
	Citric acid	3.	"
	Potassium bromide	0.5	part,
	Water	480.	parts.

Heat the water to about 65° C., then add the sulphite and the hydroquinone. When dissolved let cool and add the other chemicals.

B.	Sodium hydrate	10.	parts.
	Water	480.	"
C.	Solution of potassium bromide 1:10.		

For normal exposure.—Take 2 volumes of A, 1 volume of B, dilute with 1 volume of water; then, according as the image comes out, add gradually 1 volume of B.

For short exposure.—Mix equal volumes of *A* and *B*; then, according to circumstances, add more of *B* or dilute.

For instantaneous exposure.—Take 2 volumes of *B* and 1 volume of *A*; then, add gradually more of *A*, or dilute.

For tentative development.—Immerse in *A*, diluted with 1 volume of water; then proceed by adding small doses of a sodium hydrate solution at 1:4, or operate in the opposite manner, according to the exposure, &c.

The above method of compounding the developing solutions is, we think, more rational than that which consists to mix a new solution with an old one in proportions varying with the exposure-times, &c.

The method referred to is as follows:

A ready-made solution is prepared as follows:

Sodium sulphite	30.	parts,
Hydroquinone	5.	"
Sodium carbonate	70.	"
Potassium bromide	0.5	part,
Water	480.	parts.

This constitutes an energetic developer. It can only be employed to develop plates exposed by the drop shutter at great speed.

By use it undergoes the usual changes. It becomes colored and liable to produce a yellow fog difficult to remove; it acts more and more slowly partly from the oxidation of the hydroquinone, partly from the increasing proportion of potassium bromide, and therefore produces stronger contrasts.

To counteract the too energetic action of the new (stock) solution, one advises to mix it with a certain quantity of the old developer which, as it is seen, acts as a restrainer. For example:

For normal exposures one uses, say, 3 parts of stock solution and 1 part of the old.

For over exposure the stock and old solutions are mixed by about equal volumes.

For short exposure the proportion of the stock solution should be in great excess, &c.

Hence, the method consists to regulate the development by a judicious use of the stock solution, which leads to produce softness, mixed with the old restraining developer.

Now, the reader, by comparing this method with the simple and effective manner of conducting the development with pyrogallol, will certainly conclude that it presents no advantage but, on the contrary, leaves one in doubt about the probable action of the mixture, since the old solution is always undergoing alterations.

The following is a developer for line-works :

A.	Hydroquinone	8 parts.
	Sodium sulphite cryst. .	40 "
	Potassium bromide . . .	2 "
	Water	480 "
B.	Potassium hydrate .	6 to 8 parts.
	Water	480 "

By equal volumes. Mix *B* by half doses.

After development the plate is rinsed under the tap; then immersed for two minutes into a solution of tartaric acid at three per cent of water, and then well washed and fixed.

The acid treatment before fixing has for its object to effectually prevent yellow fog.

Berkeley's fixing bath is recommended in this and the eikonogen developing process.

CHAPTER IX.

THE DEVELOPMENT WITH EIKONOGEN.

The reductive action of eikonogen is rapid, unlike that of pyrogallol and of hydroquinone, similar to that of ferrous sulphate in the wet collodion process, developing the latent image in a minute, at first without intensity and giving thereof to the inexperienced the impression that the plate has been over exposed.

As a consequence, eikonogen has a tendency to produce very soft pictures bordering to flatness, that is, pictures without sufficient contrasts.

This is not, however, so objectionable as it has been said. We think it is even advantageous, for the great desideratum in most cases is to obtain the details, then the intensity.

To prevent the tendency to flatness, a developer strong in eikonogen with a good percentage of alkali and restrained as soon as the image is wholly visible, should be employed. In fact, the restrainer, KBr, is generally useful to avoid fogging, especially with very rapid plates.

To obtain better details when the exposure-time is short, some authors recommend to immerse the plate for a minute in the following bath before developing, then to proceed without washing the film:

Sodium thiosulphate 1 part,
Water 2000 parts:

When dissolved add—

Mercuric chloride sol., 1:25, . 5 to 10 parts.

We discard this preliminary treatment.

Eikonogen is a very good developer for drop shutter exposures.

As previously said, it develops the whole picture at once, so to say, bringing out the details in the shadows rapidly and before the lights get much intensity and, indeed, that is a

great quality; but, then, it intensifies slowly in comparison to the starting action. To intensify quickly and to obtain brilliancy the writer has recourse to pyrogallol which, when all the details are well defined and only then, is added by small quantities to the developer; or the plate may be treated by a separate pyrogallol developer compounded to produce opacity.

The drawbacks of eikonogen are its liability to produce fog* and its exceedingly rapid action in cases of unexpected over exposure-times. It is true that the action can be checked by dilution, adding potassium bromide or neutralizing part of the alkali with citric acid, but then the results are seldom as good as when the image is developed with pyrogallol.

Yellow fog occurs with eikonogen by using large doses of alkalies without the correspond-

* When the exposure-time is short the reagent, finding a weak impression to work upon, is liable to extend its action—especially when the development is slow—on the parts not acted on by light and thus produce fogging. Therefore we advise for instantaneous (short) exposure-times a very energetic eikonogen developer containing a small dose of potassium bromide. This observation also applies to any developer.

ing percentage of sodium sulphite, or by long development, or by employing an oxidized developer. The fog is sometimes dichroic—green by reflection, rose or pink by transparency—and results from the same cause which produces it with pyrogallol and hydroquinone: the dying of the gelatine film. The remedies are, consequently, the treatment with an acid clearing-solution without alum before fixing, and fixing in the thiosulphate—acid sulphite bath. The following clearing solution may be used:

Sodium sulphite	25	parts.
Sulphuric acid	5	"
Water	100	"

The color of the clichés developed by the reagent in question is a grey-black favorable for rapid printing, but requiring to push the development a little more than with pyrogallol.

To develop, prepare—

A. Sodium sulphite, cryst.	30	parts.
Eikonogen, cryst. and powdered,	13	"
Citric acid	3	"
Potassium bromide	2	"
Water	480	"

Eikonogen is slowly soluble in cold water. It should be dissolved in water heated to 35°–38° C., and after sodium sulphite.

B.	Sodium sulphite, cryst.	.	.	100	parts.
	Potassium carbonate, pure	.		120	"
	Water	.	.	480	"

For normal exposure-time, mix—

A	.	.	.	4	volumes,
B	.	.	.	1	volume,
Water	.	.	.	3	volumes.

For over exposure-time mix, in the same proportions, and restrain.

For short exposure-time (drop shutter at medium speed), mix—

A	.	.	.	3	volumes,
B	.	.	.	1	volume.
Water	.	.	.	1	"

For very short exposure-time (drop shutter at rapid speed), mix—

A	.	.	.	3	volumes,
B	.	.	.	1	volume.

For instantaneous exposures, prepare—

A ¹ .	Sodium metabisulphite	5.	parts.
	Eikongen, cryst. and powd.	6.	"
	Water	150.	"
B ² .	Sodium hydrate	5.	parts,
	Potassium bromide	0.25	"
	Water.	30.	parts.
	Mix.		

This constitutes an exceedingly energetic developer. It may be diluted with 1, 3, 5, volumes of water according to the exposure-time, &c. To obtain contrasts, add bromide; to obtain vigor when the details are out, have recourse to pyrogallol.

The developing solutions can be employed to develop several images, yielding, then, more intensity, for the reasons before explained. They are consequently good for developing plates over exposed, to obtain contrasts, &c. For short exposure-times new solutions are, as usual, recommended.

To accelerate the intensification and obtain more brilliancy, &c., the following pyrogallol solution can be added to the eikonogen developer as it has been directed :

Sodium bisulphite	1 part,
Pyrogallol	2 parts.
Water	3 "

The writer here states once more that the above proportions, good in ordinary circumstances, should be altered, as well as all others, to meet certain cases. The rules laid down for developing with pyrogallol stand necessarily good, no matter what is the reagent employed.

By experimenting, the reader will soon ascertain by himself that eikonogen and hydroquinone do not permit one to modify the development as readily and effectively as does pyrogallol which, of all the reagents employed or proposed for use to the present day, possesses the greatest elasticity of action; and, by referring to the generalities on the behavior of each of them, he will be able to apply their special properties to the best advantage without the necessity of our further consideration on this subject.

CHAPTER X.

DEVELOPMENT WITH FERROUS OXALATE.

Four stock solutions are employed to compound the developers, viz:

A.	Neutral potassium oxalate, .	200 parts,
	Potassium bromide.	1 part,
	Water	600 parts.

If this solution shows an alkaline reaction to test paper it should be slightly acidified with oxalic acid.

B.	Ferrous sulphate	60 parts.
	Sugar, white	15 "
	Tartaric acid	2 "
	Water, ordinary	200 "

The solution keeps well owing to the organic matters which by being oxidized through the ferric salt as it forms reduce it to ferrosum.

Should it become turbid a small quantity of tartaric acid must be added and the solution exposed to light.

C.	Potassium bromide	1 part,
	Water	10 parts.
D.	Sodium thiosulphate, (hyposulphite)	1 part,
	Water	1000 parts.

The solution *D* is the accelerator ; *C* is the restrainer.

The effect of *D* is almost instantaneous ; the details, which otherwise it would be impossible to force out when the exposure-time is short, appears simultaneously with a slight veil covering the picture. If added in too great a quantity it produces a dense fog and the picture is spoiled past remedy. One per cent of the developing solution is the maximum dose.

A saturated solution of potassic ferrous oxalate is prepared by gradually adding 1 part of *B* to 3 parts of *A*, *not the reverse*. It constitutes the most energetic developer which can be made with this salt. It should be prepared just before use, its energy diminishing sensibly from oxidation in contact with the air and during the development by the accession of potassium bromide.

Under the action of this compound the

image, when the exposure is right, appears within 15 or 20 seconds. The high lights first make their appearance and then the half tints.

If the plate is over exposed, the image flashes out soon after its immersion in the developer and the half tints come out almost simultaneously with the high lights. The action should then be restrained at once and the developer diluted.

On the other hand, if the high lights do not appear within 30 seconds, or if the half tints hang back, which indicates a short exposure-time, *D* is added, but only when the image shows a commencement of development, unless the operator knows that the exposure-time is very short, when the plate may be immersed for an instant in a very diluted solution of *D* (5 to 10 per 1000) and then, without washing, placed in the developing solution.*

* Audra.

By compounding the accelerator with potassium bromide as in the following formula, larger doses can be added either to the developing solution or to the preliminary bath, say, from 3 to 4 per 100. The cliché is less liable to fog on account of the small quantity of bromide, therefore more clear and brilliant images are obtained :

Sodium thiosulphate	1 part,
Potassium bromide	2 parts.
Water	480 "

As usual with the other reagents, it is advisable to commence the development with little iron and to gradually increase the dose, but without exceeding the proportion of 1 *B* to 3 *A*, and observing that a solution weak in ferrous oxalate tends to produce more contrasts.

The following formulas are given as examples, no account being taken of the lighting:

For normal exposure, commence with 12 *A* and 3 *B*. (Maximum of *B*, 4.)

For over exposure, use in the same proportion as for normal exposure and restrain.

For slightly short exposure, use 15 *A* and 4 *B*; then add *D* to obtain details. (Maximum of *B*, 5.)

For short exposure, 3 *A* and 1 *B*; then add *D*.

All these developers should have an acid reaction, else they produce fogging.

Observe that in this as in the other developing processes heat accelerates the action and tends to force out the details which hang back, and that by employing the same solution to develop 2, 3, 4 clichés, the development proceeds more and more slowly and the contrasts increase.

To reduce to ferrosum the ferric oxalate formed during the development which, more than the bromide, impairs the reductive power of the reagent, add a little tartaric acid to the solution and expose it to sunshine for a few hours, until the dark red color of the liquid turns to a ruby tint. The developer is then ready for use. As the bromide resulting from the reduction of the silver salt still restrains the energy of the regenerated ferrous oxalate, it is useful in order to obtain soft clichés to counteract this action by adding a small quantity of the accelerator *D*. This will be practically effective so long as KBr is not in too great a proportion.

In order to prevent the oxidation of a ready made developer it has been advised to compound it with some sodium sulphite, that is, a permanent deoxidizer, thus :

<i>E.</i>	Solution <i>A</i>	100 parts.
	Sodium sulphite cryst.	.			6	"
<i>F.</i>	Solution <i>B</i>	33 parts,
	Tartaric acid	1 part.
				Mix.		

When developed, the plate is washed, cleared

in a solution of *citric acid*, washed again, then fixed, &c.

The color of the clichés developed with ferrous oxalate is a grey or bluish-black—very favorable for rapid printing and transparencies.

The writer of this work thinks that ferrous sulphate is the *best developer in microphotography* on account of the fineness of the silver deposit and the freedom from fogs and stains.

Pyrogallol cannot be employed with ferrous oxalate, a black precipitate is formed.

CHAPTER XI.

§ 1. DEVELOPMENT WITH PYROCATECHIN.

Pyrocatechin was introduced for the development of collodion clichés by Mr. R. Wagner, in 1859. Lately Dr. J. M. Eder applied it to the gelatine process. The formula published by the learned doctor is the following:

A.	Pyrocatechin	1 part,
	Sodium sulphite	4 parts.
	Water	50 "
B.	Potassium carbonate	4 parts.
	Water	40 "
	Mix 1 of A to 2 of B.					

This developer acts more rapidly than hydroquinone, permits to lengthen the development, and yields, clear clichés free from fog and having fair printing qualities.

It is little employed, and in our opinion presents no serious advantages over pyrogallol.

§ 2. DEVELOPMENT WITH HYDROXYLAMINE.

A.	Chlorhydrate (chloride) of hydroxylamine	30 parts.
	Alcohol	480 "
B.	Caustic potash	60 parts.
	Water	480 "
C.	Potassium bromide	20 parts.
	Water	480 "

"To develope, take 30 parts of *A*, 40 parts of *B*, and 10 parts of *C* diluted with 480 parts of water the development proceeds rapidly and is completed in about five minutes.

"The advantages claimed are : wide latitude of exposure, non deterioration of the solution from external sources,* and absolute freedom from fog or stains—a gain that cannot be too strongly accented.

"Against these important advantages I should state that there is a minor objection, and that is the liability to cause recticulation from the softening of the film by the caustic

* Hydroxylamine does not absorb oxygen from the air in presence of alkalies.

alkali and the evolution of nitrous oxide from the decomposition of the hydroxylamine.”*

The tendency to frilling which Mr. Spiller speaks of is not entirely peculiar to the process; with certain brands of plates it occurs, whatever be the reagent, if it is compounded with large doses of strong alkalies. However, in this process the defect is not always avoided even by adding a little alcohol to the developing solution or using less alkali, for it is mostly due to the nitrous oxide evolved during the decomposition of hydroxylamine.

This process is little employed, requiring a longer exposure-time than pyrogallol to obtain the same intensity, and being prone to produce blistering as previously stated.

§ 3. DEVELOPMENT WITH PARAMIDOPHENOL.

“Paramidophenol,” says Messrs. Auguste and Louis Lumière, who applied the reductive properties of this compound to the develop-

* Arnold Spiller.

ment of the photographic image,* "in presence of a base or of an alkaline carbonate possesses remarkable reductive properties which render it valuable as a developer."

The reduction of the silver bromide is effected in the ordinary manner.

Water is decomposed; the oxygen is absorbed by Paramidophenol with formation of quinonimide (or quinone) while the hydrogen reduces the silver bromide by uniting to the haloid.

Paramidophenol is the product of the action of tin and hydrochloric acid on paranitrophenol. It crystallizes in plates which melt at 184° C. in being decomposed. At 0° C. it dissolves in 90 parts of water and in 22 parts of absolute alcohol. Formula :



The solubility of paradiphenol is not much increased by the temperature.

The aqueous solution oxidizes in the air assuming a violet-red tinge especially in presence of the alkaline bases with which paradi-

* Bull. Assoc. Belge Phot., Vol. XVIII, p. 435 *et seq.*

phenol combines in forming salts possessing powerful reducing properties. (Andressen.)

The following formulas answer well for the development of gelatino-bromide of silver plates:

Paramidophenol . . .	12 parts.
Sodium sulphite . . .	200 "
Sodium carbonate . . .	100 "
Water	1000 "

or—

Paramidophenol . . .	12 parts.
Sodium sulphite . . .	200 "
Lithium carbonate . . .	12. "
Water	1000 "

The first formula forms a very energetic developer which answers for plates instantaneously exposed.

As a developer paramidophenol presents the inconvenience of not being sufficiently soluble, so that it is not possible to make in the constitution of the developer as many modifications as those possible with a very soluble body such as pyrogallol.

Hydroquinone and eikonogen also present this inconvenience to the same degree, but paramidophenol possesses over them, hydroquinone especially, the advantage of never coloring the gelatine.

The solution keeps for a long time, even in uncorked vials, and the clichés developed by an old bath are free from that yellow fog often occurring when using other developers.

The action of the paramidophenol developer is, by use, very slowly exhausted, and this to such a point that in 100 grams of solution one can develop 6 or 7 plates 13x18 c. m. without any appreciable difference between the first and the last.*

Lately Messrs. Lumière have published the following formula as working better than those they had first given :

Water	800	parts.
Potassium carbonate . .	40	"
Sodium sulphite . . .	100	"
Paramidophenol . . .	8	"

Andressen compounds the developer as follows :

Hydrochloride of paramidophenol	5	parts.
Sodium sulphite cryst.	50	"
Potassium hydrate	25	"
Water	1000	"

* Here, especially, we do not agree with the inventors. The alkaline bromide, the proportion of which increases with every plate developed exerts its action with the usual results, as also the various doses of alkali.

PART III.

THE DEVELOPMENT IN THE NEGATIVE AND
POSITIVE COLLODION PROCESSES, AND
IN THE SILVER BROMIDE
PRINTING PROCESSES.

CHAPTER I.

THE DEVELOPMENT IN THE COLLODION PROCESS.

In the collodion wet process the image is developed by a solution of ferrous sulphate acidified by acetic acid: the silver nitrate in excess on the photo film being reduced by the salt of iron precipitates with adherence upon the impressed parts and forms the image. During the action the silver film is not altered, for if the image be dissolved by nitric acid, or, as shown by Mr. Carey Lea*, by mercuric nitrate, it is possible to take upon it another impression by the same means. It is well known that ferrous sulphate does not act on the silver haloids.

It is, indeed, a very remarkable phenomenon that the change, generated by the dynamic

* Phil. Photographer, 1865 and 1886.

action of light in the molecular state of the silver haloids previously to the dissociation of the elements, which causes them to be reduced by a chemical developer,* also exert an attractive action on metallic silver in a state of nascent reduction, and that, proportionally to the degree of insolation, so that the silver atoms are attracted with more or less energy and consequently precipitate in more or less quantities, thus forming an image in gradation of tints; the reader remembers that by the alkaline method of development the image is formed by the silver reduced from the photo film itself.

The reduction of silver nitrate by ferrous sulphate is rapid. Almost as soon as the developing solution is flowed on the impressed photo film the image appears and is wholly developed in less than one minute. It is not, therefore, possible of regulating the develop-

* This term is applied to the developers which reduce the impressed silver haloids, alkaline pyrogallol, ferrous oxalate, hydroquinone, etc., to distinguish them from the acid or *physical* developers, ferrous sulphate, ferrous nitrate, etc., which do not act on these salts and cause the development of the image by reducing the silver nitrate as here explained.

ment as with a chemical developer whose action is gradual and slow: other means should be resorted to in order to obtain either softness or vigor.

These means are: the constitution of the collodion, the state of the silver bath, the exposure-time, the more or less energy of the developing solution, the redevelopment and intensification.

This work having for its especial object to guide the student in the operations of the development, we shall not describe how to make a suitable collodion to obtain soft or brilliant images, nor shall we enter into the description of the causes which impair the silver bath, of the manner of restoring it to working order, nor give a detailed list of the failures occurring in the process. For instructions on these matters we refer the reader to treatises on general photography. However, we will state, incidentally, that to obtain intensity the collodion should be thick and well bromo-iodized, and the same diluted for soft pictures—portraits, for example.

In the wet collodion process, the exposure-

time is one of the most important factors, since the development is almost purely mechanical. When the time is short no details are obtained in the deep shadows, if the plate is over exposed, the image is grey, too uniform and liable to fog. However, it is advantageous when the subject is in half-tones to somewhat over expose, because by reducing or intensifying—to which we are often obliged to resort in this process to obtain a good printing general intensity—more contrasts are always the result.

Compared to gelatine, the exposure should be about ten times longer than the plates of ordinary rapidity, say 20 Warnerke.

The developer for the wet collodion process is compounded in four different manners, viz:

1. *Normal Developer.*

Ferrous sulphate	30 parts.
Acetic acid No. 8	40 "
Sulphuric acid	3 "
Water	480 "

This is the standard developer. It is strong and keeps well owing to the presence of

sulphuric acid preventing oxidation. A little alcohol should be added to it when it does not flow well.

2. Energetic Developer.

Ferrous sulphate	40 parts.
Acetic acid No. 8	30 "
Glucose	20 "
Copper acetate	2½ "
Water	480 "

This developer should be prepared several hours beforehand and heated to 25° C. for use. It develops rapidly, yielding soft negatives full of details. The silver bath should be acidified with acetic acid, C. P.

If, instead of acetate, 1½ parts of sodium formate and 3 parts of formic acid are added, the most powerful developer employed in the wet collodion process is obtained.

3. Weak Developer.

Ferrous sulphate	15 to 20 parts.
Acetic acid No. 8	45 "
Sulphuric acid	2 "
Water	480 "

**4. Developer for Line-works.
(Engravings, Etc.)**

Ferrous sulphate	25 parts.
Tartaric acid	4 to 5 "
Water	480 "
Alcohol	quant. suff.

This developer kept in the light does not oxidize. It acts slowly. The image appears in from 20 to 30 seconds and then gradually intensifies. Generally the blacks are very intense and the whites (clear glass) free from silver deposits, which is of great importance when the cliché should be intensified and used in photo-engraving.*

It must be observed that a weak developer, that is, working slowly, tends to give contrasts, while a strong developer such as 1 and 2 promotes softness in securing details. Here again the rule before laid down holds good: to obtain gradation, the details should be brought out before the high lights get intensified.

* We advise the reader to use with this developer a collodion compounded with zinc iodide and bromide, thus:

Sodium iodide	5 parts,
Zinc iodide	1 part,
Zinc bromide	1 "
Collodion, plain	480 parts.

The plain collodion should be made with a pyroxiline prepared at a high temperature and have a good body. This iodo-bromized collodion does not keep well. It is best to have the iodides and the bromide in separate solution and to mix by quantities sufficient for about a week's use.

The silver bath should be acidified with nitric acid chemically pure.

To develop, the plate is placed on a stand held in the left hand and the developer flowed over the film from the lower edge of the plate with a gentle sweep from left to right so that the liquid runs in one even sheet and covers the whole film at once. During the development the liquid should be kept in motion taking care that every part of the film be alternatively washed.

At this stage of the operation one can judge whether the exposure-time is right. When it is short the image appears slowly and the details in the shadows refuse to come out, whilst in the case of excess of exposure it flashes out instantly in all its parts but without sufficient contrasts. The development of well exposed plates, although quite rapid, proceeds gradually.

The action of the developer is exhausted in a minute and if the exposure-time is sufficient, the development does not require more than about half that time to bring out the faintest details in the shadows; then the film should be washed under the tap and fixed.

The failures from the development arise from

the irregular flooding of the plate. They appear as streaks and markings which are avoided by observing—

1st. Not to flow the developer from the lower edge of the plate before the latter has been drained on blotting paper, for the silver solution there accumulated during the exposure-time may be carried irregularly over the film and form streaks of intensity;

2nd To flow the developer in an even stream, so that it does not divide in several rivulets, because the silver solution pushed on the film by these various streams accumulates at their point of junction and there determinates markings of opacity

3rd. To avoid pouring violently the developer on the film. In this case hair lines are usually formed, radiating from the place the developer has been poured on.

These hair lines are sometimes also produced by strong developers, that is, containing large proportions of ferrous sulphate. This especially happens in reproducing subjects on a white ground. The remedy is obvious.

4th. Lastly, not to pour the developer steadily on one spot, as the silver nitrate being

thus washed away, the negative remains there more transparent than on the other parts.

The clichés are intensified either by *Re-development*, or by chemical actions similar to those employed in the gelatine process and classified under the title of *Intensification*.

RE-DEVELOPMENT: The re-development is especially adapted for half tone subjects. It is done in the dark room just after the development proper, in order to preserve the most delicate shades and details which may be dissolved by the fixing agent, potassium cyanide.

As the name indicates it, this operation is nothing else than the continuation of the development. It is effected by treating the cliché, well washed, by a solution of pyrogallol to which is added a small quantity of a silver nitrate solution :

A.	Pyrogallol	1 part.
	Citric acid	2 parts.
	Water	480 "

B.	Silver nitrate	15 parts.
	Water	480 "

It should be observed not to increase the general intensity beyond that absolutely necessary to obtain good prints, because the image does not preserve the same relation between the high lights, the half lights, etc., but increases in contrasts, the silver being deposited in greater quantities on the parts where there is already a denser layer of metal. It may be said that the affinity of silver in the nascent state of reduction for the metal forming the image is in the ratio of the mass deposited during the development.

It sometimes happens that by re-developing after fixing, an inverse action takes place, the negative being converted into a positive. This effect which commences to manifest itself by a reddish reduction in the deep shadows and at the edges of the cliché, is avoided by flowing the plate with a solution of iodine or of mercuric iodide in sodium iodide and washing before applying the re-developing mixture. The solution of mercuric iodide must be weak and allowed to act for two or three seconds.

A stock solution of potassic mercuric iodide may be prepared by adding gradually to a solution of potassium iodide, 4:100, another

of mercuric chloride (saturated) until the red precipitate formed does no more dissolve.

The re-development with ferrous sulphate recommended by some authors is not so effective as that with pyrogallol, nor so great an intensity can be obtained. But it sometimes brings out details not fully developed on account of the rapid reduction of silver nitrate by ferrous sulphate. For line works it is objectionable, for the lines are liable to be blocked up by a deposit of silver.

This developer consists of a solution of from 8 to 10 parts of ferrous sulphate and half the quantity of citric acid in 480 parts of water, to which, for use, is added a little of the silver nitrate solution whose formula is above given.

The mixture is flowed on the cliché just after developing and washing.

INTENSIFICATION: In the collodion process, either wet or dry, the intensification is employed for clichés in lines, not for those in half tones, for the medical action is rapid and cannot be well controlled.

Many processes can be employed to intensify line clichés. We will describe the most em-

ployed—those of Prof. Ad. Martin, of Dr. Eder Toth, and of Wm. Cambell.

1st. *Professor Adolph Martin's process* (1861).*—When the image is fixed † and well washed it is treated by a plain solution of bichloride of mercury until uniformly whitened. It is then carefully washed and a solution of double cyanide of silver and potassium is poured over. This solution is prepared by adding to a 10 per 100 solution of potassium cyanide a saturated solution of silver nitrate until the precipitate formed is no more dissolved by agitation. The liquid is then filtered and a very small excess of potassium cyanide is added. Instead of silver nitrate, the copper salt can be used ; the result is the same.

The metal precipitated by the chemical action is black and increases the intensity of the negative.

This process may be used for toning diapositives.

Sodium thiosulphate (hyposulphite) may be

* This process has been wrongly attributed to Dr. Monckhoven by English authors. Old processes are often revived without giving the honor of the invention to whom it is due.

† It should be fixed by potassium cyanide.

substituted for potassium cyanide and the solution prepared in the same manner, but not in great quantities—it does not keep.

The cliché should not be fixed after this operation; it suffices to wash it well.

By repeating over these operations, the negative can be intensified to any desired extent without risk of any reduction being formed in the transparent parts if they are clear from reduced silver.

*William Campbell's process (1876).** *For line works*—Into a saturated solution of sulphate of copper pour a solution of bromide of potassium enough to turn the color of the negative to a white.† This may be done either by pouring off and on several times the solution, or leaving the plate in a dish till the color changes (bleaches); the stronger the bromide in the solution, the quicker will it change.‡

* This process has been wrongly attributed to Captain Abney.

† The following solution may be employed:

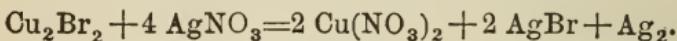
Potassium bromide	3 parts.
Cupric sulphate	6 "
Water	120 "

‡ Cuprous and argentic bromide are formed. (See further on.)

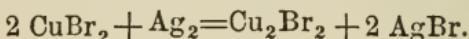
When this stage is obtained, wash the plate and pour on a dilute (2 : 100) solution of silver nitrate ; the film will now become denser, and black. If not dense enough repeat the operation.* It is rarely necessary to go further ; but if any disappointment is experienced, it is a sure sign of derangement in the (sensitizing silver) bath—perhaps, too weak.†

For portraits and similar works it is not

* The chemical actions are represented thus :



† Whatever be the intensifying process employed, it is necessary, in order to obtain opacity, that the image be formed by a certain quality of metallic silver, that is, not too weak, since the result of the chemical action depends upon the thickness of the layer of this metal. In the process we describe the changes taking place by treating the cliché with cupric bromide are as follows :



Hence the amount of cuprous bromide reacting with silver nitrate to obtain intensity is proportionate to that of the metallic silver originally forming the image. If the image is weak, we advise the operator to re-develop it before intensifying.

It is always very important, before intensifying clichés from engravings, etc., that the lines be clear, that is, free from any deposit of silver ; the reason is obvious. If the lines were partly blocked up, no matter how little the silver deposit, they should be cleared by treating the cliché with a solution of iodine in potassium cyanide (cyanide of iodine). The solution should be diluted and applied with care for it rapidly dissolves the metal.

necessary to carry the treatment with mercury to the white stage, simply pouring alternatively the solutions and washing well the plate, till the required intensity is sufficient.

Dr. Eder and Toth's process (1876).

Red prussiate of potash	30 parts.
Nitrate of lead	20 "
Distilled water	488 "

Distilled or rain water should be employed. Any water containing lime will cause a precipitate all over the negative.

The negative is dipped into this bath or it may be flowed over it as soon as it is fixed and well washed. During the action of the lead bath there is deposited on the silver parts of the picture a faint yellowish-white precipitate which makes the film appear quite white and possesses an extraordinary amount of intensity. It is necessary to let the negative remain in the bath until it has assumed the same amount of density which you require in the end, for the after treatment with ammonium sulphide is rather for the purpose of rendering the reduction permanent than to change the density.

After the negatives have been taken out the lead bath and well washed with distilled or rain water, the following solution is applied:

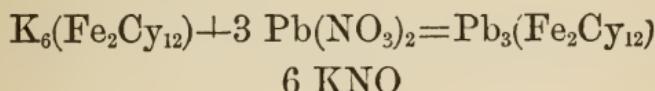
Ammonium sulphide	30 parts
Water	480 "

Immediately upon this application, the image becomes perfectly black and, when the reduction is blackened right through, the sulphide is washed off with ordinary water, the result being perfectly transparent lines upon a coal-black ground.

This method produces a more dense ground than the bichloride of mercury process generally employed by photo-engravers, and it has this advantage that the lines are not easily covered. However, greater intensity for negatives from engravings and the like will be obtained by treating them first with the lead solution, then with iodide of iron and, lastly, after a thoroughly good washing, with permanganate of potash. The negatives assume by this process a deep brown-black and the lines remain quite clear.

This intensifying process is based on the following chemical actions:

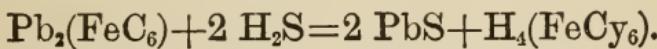
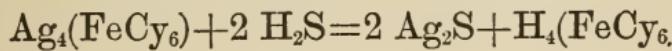
Potassium ferricyanide and lead nitrate form lead ferricyanide—



Lead ferricyanide in presence of silver converts it into ferrocyanide, and being itself transformed to a similar salt deposits on the former:



Now these two salts, silver and lead ferrocyanides by being treated with ammonium sulph-hydrate are decomposed with formation of silver and lead sulphites:



CHAPTER II.

THE DEVELOPER IN THE DRY COLLODION PROCESS.

Collodion dry plates are prepared either by the bath or emulsion process. To prepare by the bath process the plate is coated with a bromo-iodized or, simply, bromized collodion, then sensitized, washed and flowed with a preservative—tannin, gallic acid, etc.—which plays the part of a sensitizer.

The latent image is developed by a physical or a chemical developer. If the photo film consist of silver bromo-iodide in the proportion usually employed in the wet process, $4\text{ NaI} : 2\text{ CdBr}$, the image seldom acquires a sufficient general intensity for, as previously stated, silver iodide is almost inert under the action of the latter (alkaline) developer. Therefore, in this case the image should be redeveloped

after acidification to neutralize the alkali and a thorough washing.

The development by a physical developer is preferably employed for transparencies and sometimes for bromo-iodized plates prepared by the bath process. It is as follows :

After exposure the plate is wetted under the tap, then flowed with a solution of, say, 120 parts of water and 2 parts of an alcoholic solution of pyrogallol at 1 : 5, which is allowed to act for one or two minutes, when it is poured off in the developing cup and, a few drops of the following silver solution being added, flowed back on the film :

Silver nitrate	120 parts.
Citric acid	60 "
Water	480 "

In a few seconds the image commences to appear, and when the details in the shadows are well out, more of the silver solution is added to obtain intensity.

Starting the development with much silver nitrate is always injurious. The high lights acquire too much intensity before the details are sufficiently developed.

The chemical or alkaline development of

collodion dry plates is, of course, conducted as in the gelatine process. We will, however, give an example, observing that the bromide is not only useful to control the development, as first pointed out by Major C. Russell, but also to prevent fogging. In the dry collodion process it is a *sine quâ non*, for the nitro-cellulose film does not, as gelatine, acts as a restrainer.

A.	Ammonium sesquicarbonate,	50 parts.
	Water	480 "
B.	Potassium bromide	10 parts.
	Water	480 "
C.	Pyrogallol	25 parts.
	Water	480 "
D.	Aqueous ammonia conc. .	50 parts.
	Potassium bromide . .	10 "
	Water	480 "

To develop, immerse for a minute the plate in alcohol diluted with two or three volumes of water, then in water until the liquid is no more repelled. Now take 3 parts of *A*, 1 part each of *B* and *C* and dilute with 12 parts of water; flow this mixture on plate well drained: if the image gradually appears in all its details, let the action proceed until the latter are well

out and, if then the image does not become sufficiently intense, increase the dose of *A* and *C*. When, on the first application of the developer the image does not appear within 20 or 25 seconds, add from 1 to 2 parts of *A*. Should the details hang back—the exposure-time being then most likely short—add a very small quantity of *D*.

On the other hand when the image flashes out, either wash the plate immediately and proceed to develop with a solution containing less alkali and more pyrogallol and bromide, or restrain by adding more of *B* to the original solution.

Another method of developing, also employed for gelatine plates is the following:

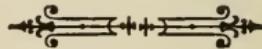
On its removal from the holder the plate is immersed in a solution of pyrogallol and, for collodion dry plates, of a small quantity of potassium bromide, say—

Pyrogallol	from 1.5 to 2. parts,
Potassium bromide, (maximum)	0.5 part,
Water	480. parts.

to which can be added a certain quantity of sodium sulphite.

In this the film is allowed to soak for one or two minutes, when 20 parts of a solution of crystallized sodium carbonate saturated at 15° C. are added. If the image appears in a short time, the plate is well exposed and the development allowed to go on; if it hangs back, the dose of sodium carbonate is increased by successive additions of 10 parts until the details are out; and if then there is any tendency that the image develops too uniformly, one should increase the dose of pyrogallol and that of potassium bromide. This is a tentative method. The operation can be reversed when the exposure-time is short or the subject lighted by strong oppositions, as before explained.

Clichés on collodion dry plates are fixed with sodium thiosulphate 1:8, not with potassium cyanide unless developed by the silver-pyrogallol process.



CHAPTER III.

THE DEVELOPMENT OF FERROTYPES.

The ferrotypes, or direct positives on collodion films are, in fact, weak negatives, made by under exposing and under developing. Seen by reflection, the lights which are formed of metallic silver appear white, whatever be the backing, and the half lights being more or less transparent on account of the thin layer of reduced metal, have no other value than that of the backing itself, which may be black, brown-black, &c.

Developer No. 1.

<i>A</i>	Ferrous sulphate	50	parts.
	Sugar, white	15	"
	Water	480	"
<i>B.</i>	Lead nitrate	18	"
	Water	480	"

Mix, let settle the precipitate, filter, then add acetic acid No. 8, 40 parts, alcohol 10 parts.

This developer yields fine dead-white tones.*

Developer No. 2.

Ferrous sulphate . . .	15 parts.
Potassium nitrate . . .	10 "
Acetic acid, glacial . .	20 "
Alcohol	20 "
Water	480 "

"This developer allows the image to be fairly visible before it is thrown off, taking in cold weather nearly a minute to bring out and allowing the draperies to be seen."†

The silver reduction is lustreless, but not quite as white as with the above developer.

Some operators add half a part of nitric acid and 30 parts of No. 8 acetic acid instead of the expensive glacial acid.

Developer No. 3.

A. Ferrous sulphate . . .	72 parts.
Water	384 "
B. Barium nitrate	48 parts.
Water	384 "

Dissolve in warm water, mix, filter, then add from 2 to 4 parts of nitric acid and 48 parts of alcohol.‡

* P. C. D. 1853.

† John Spiller, 1855.

‡ Keith, 1857.

Mr. Keith—whose pictures are remarkably good, recommends a strong, fully iodized collodion containing *bromine** and a silver bath at 8 per 100 acidified with acetic acid chemically pure.

By substituting 24 parts of No. 8 acetic acid† for nitric acid the reduction is dead-white and the developer acts with greater energy. As prepared by Mr. Keith it is feeble; 7 to 8 parts of ferrous sulphate may be added in cold weather with advantage.

These developers are employed by very few ferrotypists although giving better results than the following, generally recommended in modern treatises :

Ferrous sulphate	20 parts.
Acetic acid No. 8	30 "
Water	480 "

We advise the reader if he selects this developer to add 2 parts of alum and a little sugar candy to it.

Mr. Victor Petit states (1855) that by adding

* That is, a few drops of a diluted solution of brom-hydric acid.

† 24 parts of alcohol are then sufficient.

to the above solution 1 part of pyrogallol, clearer proofs and purer whites are obtained. For the same purpose Mr. E. M. Estabrook has recommended (1878) a little tannin added just before developing.

Developing formulæ with sulphuric acid to prevent the oxidation of ferrous sulphate and consequently the formation of a basic ferric sulphate which precipitates with the silver and impairs the *éclat* of the metal are often given. Theoretically this is quite correct, but in practice the whiteness of the lights is thereby little, if any, injured, unless the developing solution be used over again, in which case the lights take an ochreous tint.

We advise the reader to discard this acid; it gives the whole picture an inartistic metallic lustre injurious to the half tones. To prevent oxidation sugar is sufficiently effective; moreover, it acts as a physical restrainer without, however, necessitating a longer exposure.

Pyrogallol was the first developer employed in the direct positive process, but soon super-

ceded by ferrous sulphate which allows a shorter exposure to bring out the latent image.

The whites obtained by pyrogallol are beautiful—ivory-like and quite lustreless. It may be employed whenever the exposure-time can be a little lengthened without inconvenience:

Pyrogallol	3 parts.
Nitric acid (maximum)	1 part,
Water	480 parts.
Alcohol	quantity sufficient.

To photograph by the ferrotype process, place the model in a soft, subdued light. A strong illumination produces too much contrast in this more than in any other process.*

Expose so that the developer acts somewhat slowly, causing, however, the details in the shadows to be visible within one minute.

Before developing place for an instant the plate on its lower edge on blotting paper in order that the silver solution accumulated at the bottom of the plate be absorbed by the paper.

* See our work, "The Lighting in Photographic Studios."

CHAPTER IV.

THE DEVELOPMENT OF BROMIDE PAPER PRINTS.

On account of its great sensitiveness the bromide paper is best impressed by an artificial light which, being nearly always of the same intensity, permits one to work in similar conditions of illumination—a great desideratum, indeed, to regulate the exposure-time.

The light from a duplex petroleum lamp, or that emitted by a large size fish-tail gas burner reflected by a silvered *parabolic* mirror answers quite perfectly to print by contact or by the camera.

The light being selected one should try at what distance from it the bromide paper should be placed in order to expose for not less than twenty seconds. Rapid exposure-time is not a *sine quâ non* in this process; far

from it, it is a cause of frequent failures, since the paper being coated with a thin layer of the sensitive compound and, therefore, allowing but little latitude in the time of exposure, the least error has a great influence on the results, while by long exposures a few seconds more or less do not affect it much. This is not especial to the process, but to every other, whatever may be, after all, the nature and thickness of the sensitive compound.

When the cliché is of the ordinary general intensity, at a distance of 50 centimetres an exposure of about 20 seconds is likely correct for most of the bromide paper found in the American market; then, as the distance increases, the exposure-time also increases, but inversely to the square of the distance, according to a well known law of physics. Hence, at the distance of one metre, it should be, theoretically, 80 seconds in the case in question— $50^2 : 100^2 :: 20 : x = 80$.

The best developer in this process is without any doubt the ferrous oxalate. Three stock solutions are employed:

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A.	Neutral potassium oxalate	160 parts.
	Water, rain or distilled	480 "

To this solution oxalic acid (about 2 parts) should be added until the test paper indicates an acid reaction.

B.	Ferrous oxalate	160 parts.
	Tartaric or citric acid	8 "
	Solution C	6 "
	Water	480 "
C.	Ammonium chloride	120 parts.
	Water	480 "

To develop, immerse the paper impressed side upwards in water (rain or distilled, any water free from lime) and let it soak for a few minutes until it lies flat, then pour off the paper, prepare the developing solution by mixing 1 part of *B* to 6 parts of *A* (not the reverse) and flow it on the paper so that it be covered at once on its whole surface. If the exposure is right, the image gradually appears and gains vigor. When the half tints in the lights are visible and the general effect good, *immediately* pour off the developing solution and *without washing* or taking the print out from the tray, flow over it a solution of—

Citric acid 2 parts.

Water 480 "

This solution should be twice renewed in order to eliminate the iron salt which would impair the whiteness of the paper, the picture assuming in the fixing bath a yellowish tint. This done and after a thorough washing the print is fixed. The image loses nothing by fixing; it remains such as it was after development. Over developing is, therefore, objectionable, although the intensity may be reduced by the Monckhoven's process before described.

The fixing bath should be slightly alkaline. It consists of—

Sodium thiosulphate (hyposulphite), 80 parts.

Sodium carbonate 2 "

Water 480 "

Washing after fixing should not be done in running water, the reason is evident; but, by changing one by one the proofs from one tray to another (filled with fresh water) every fifteen minutes, whereby, in two hours, they will be sufficiently washed. The last traces of sodium thiosulphate are eliminated by a

weak solution of *eau de Javelle* and, this done, if there be any persistent discoloration in the high lights, the prints are immersed in a solution of chrome alum acidified with citric acid and then finally washed thoroughly.

The development cannot be well controlled with potassium bromide which causes the prints to be tinged green if employed in a certain quantity. Ammonium chloride, an energetic restrainer, is not objectionable ; but it tends to produce warm tones.* Sodium sulphite acts as a weak restrainer and produces black tones if added to the developer in the very beginning of the operation.

Some authors advise one to use the developer over again, that is, to develop several prints in succession. More contrasts are thus obtained, but we question whether better results are, on the whole, obtained. Vigor and brilliancy can be obtained by developing

* According to Molteni various tones can be obtained with the same developer by varying the time of exposure. Short exposure-times lead to obtain black tones and long exposure-times to obtain sepia tones. By diluting the developer various tones may also be produced.

with a weak developer—one compounded with less ferrous sulphate, and softness by using a strong one, that is, containing a larger dose of ferrous sulphate.

Necessarily weak developers are used in case of over exposure-times and *vice versa*. As to sodium thiosulphate for accelerator when the time of exposure is short, we do not advise to employ it, it being liable to produce fogging.

To test whether the exposure-time is right, one operates as usual by the tentative method. The reader knows in what the method consists—flowing first the print with the solution of potassium oxalate *A*, then adding that of ferrous sulphate *B* by degrees.

The failures are necessarily similar to those occurring in the negative gelatine process, and traceable to the same causes.

Those especially pertaining to the process are—

Harsh images.—Exposure-time too short; developer not containing enough ferrous sulphate (oxalate); the image not fully developed.

The picture too intense.—Reduce by Farmer's or Monckhoven's process on the removal of the proofs from the fixing bath and a superficial washing, just as when reducing negatives or diapositives.

Prints flat; tinted whites; greenish blacks.—Over exposure-time; long development.

To tone grey.—The development not enough pushed; or, the developer not enough restrained.

The whites yellow.—The developing solution not enough acidified. The fixing bath acid, or the clearing acid not well washed off before fixing (sulphuration).

Blistering is prevented by treating the prints after developing by a solution of chrome alum.

Stains and markings are removed by washing them with a very diluted solution of iodide of cyanogen prepared by dissolving a small quantity of iodine in a solution of potassium cyanide.

Proofs over developed or flat can be treated in the same manner and thereby much improved.

Iodide of cyanogen forms also a good clearing solution for fogs.

Iron stains are removed by soaking the prints for an hour in a solution of citric, tartaric or oxalic acid. Very pure whites are thus obtained.

Eikonogen is the best substitute for ferrous oxalate. The developing solution keeps well, is seldom liable to stain the paper yellow and yields clear images.

The following compound works well :

A.	Eikonogen	16 parts.
	Sodium sulphite	40 "
	Potassium bromide, 1.10	5
	Water	480 "
B.	Potassium carbonate	160 parts.
	Water	480 "

For use, take of—

A	480 parts.
B	30 "
Water	160 "

Formulas for the development of Anthony's bromide paper :

A. Distilled water 1000 parts.
 Potassium oxalate, neutral 300 "
 Acetic acid (to redden the blue
 litmus paper) . . . quantity sufficient.

B. Distilled water 1000 parts
 Ferrous sulphate, pure 400 "
 Sulphuric acid, C. P. 2 "

C. Rain water 100 parts.
 Potassium bromide 3 "

Developing Solution.

A 60 parts,
 B 10 "
 C 1 part.

*Formulas for developing Eastman's bromide
 paper:*

A. Water 1000 parts,
 Potassium oxalate, neutral 250 "
 Sulphuric acid (to redden the
 test paper) . . . quantity sufficient.

B. Water 100. parts,
 Ferrous sulphate, C. P. 30. "
 Citric acid 2. "
 Sulphuric acid 0.5 part.

C. Water 100 parts.
 Potassium bromide 2 "

Developing Solution.

A 100 parts.
 B 15 "
 C 2 "

CHAPTER V.

VARNISHING.

It is not absolutely necessary of varnishing the clichés on gelatine, this substance being quite hard and resistent. However, it is advisable to do so, not only to preserve them from the action of dampness and prevent mouldiness but also to shelter the silver image from any atmospheric influence which may cause it to *fade*.

Varnishing is also a protection against the various accidents which may occur in printing.

Self-drying alcoholic varnishes, that is, compounded with ammonia and, sometimes, plain varnishes, cannot be employed for negatives intensified by mercury, the intensifying compound being by place dissolved and rendering the cliché too transparent. In this case it is

advisable to use as a varnish a solution of gum arabic:

Gum arabic	1 part,
Water	8 parts.
Olive oil . . .	a few drops.

Gum arabic is also employed as a substratum to prevent the alcoholic varnish permeating the film and thus to increase the transparency of the clichés.

Alcoholic Varnish.

Sandarnac	2 parts,
Benzoin	1 part,
Shellac, brown . . .	1 "
Elemi	2 parts,
Oil of lavender . . .	1 part,
Alcohol, 95° . . .	35 parts.

This varnish must be flowed onto the plate slightly warm, then drained off and dried by heat. It forms a good surface to retouch upon.

Aqueous Varnish.

White shellac . . .	20 parts.
Aqueous ammonia, conc. 26° Baumé . .	25 "
Alcohol	25 "

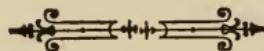
When dissolved add 70 to 80 parts of water and filter.

Or—

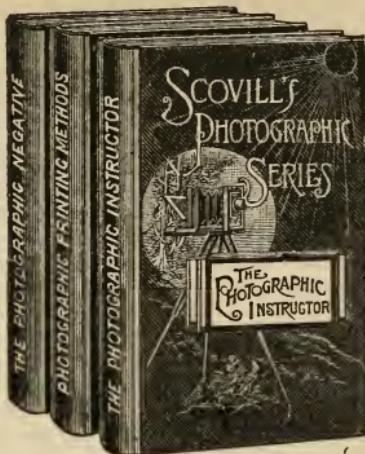
Bleached shellac . . .	32	parts.
Borax	8	"
Sodium carbonate . . .	2	"
Glycerine	1 to 2	"
Water	300	"

The cliché fixed and washed is twice flowed over with this varnish, then allowed to dry spontaneously.

END.



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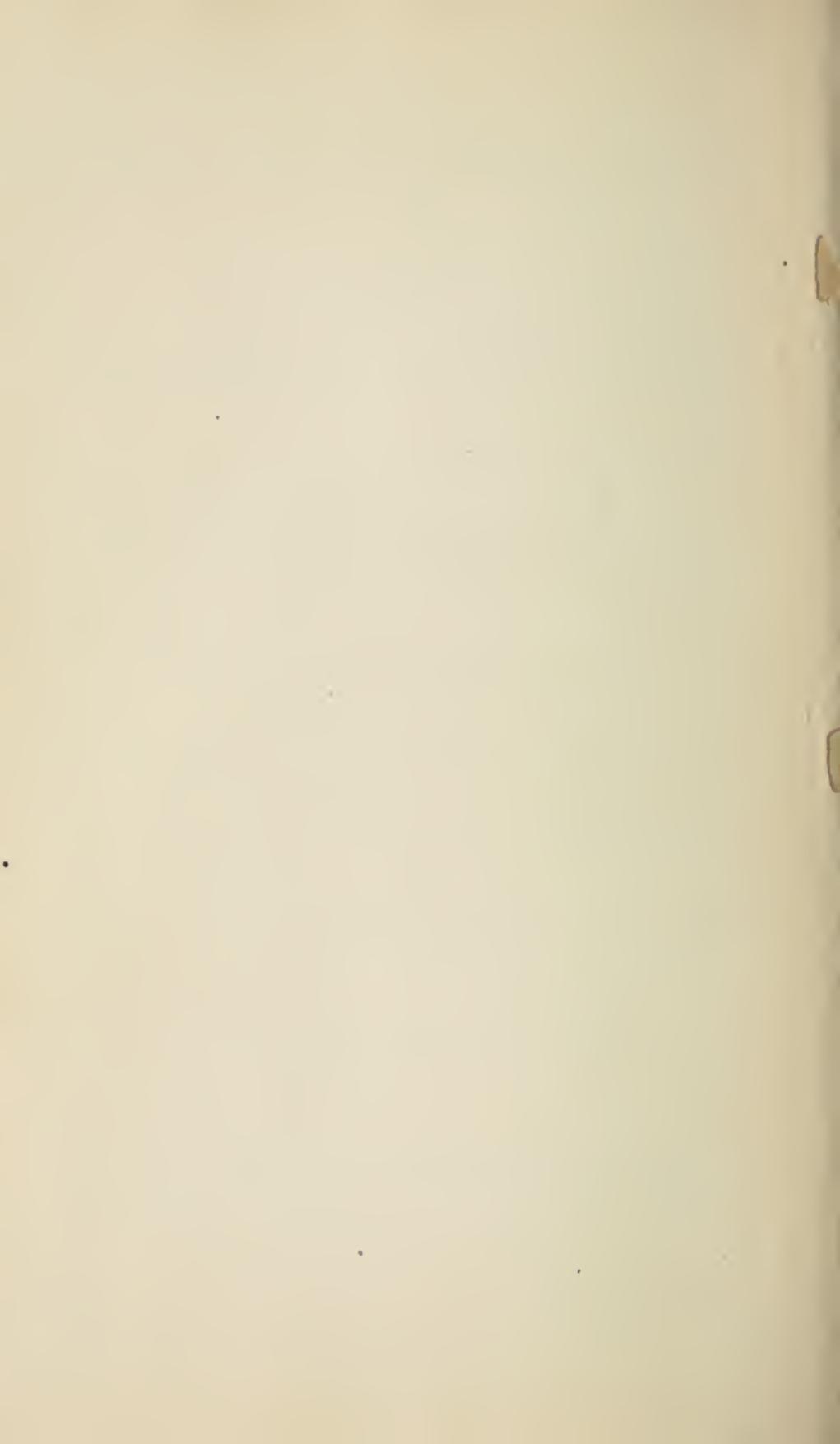
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